Luminescence of lanthanides and phosphor applications

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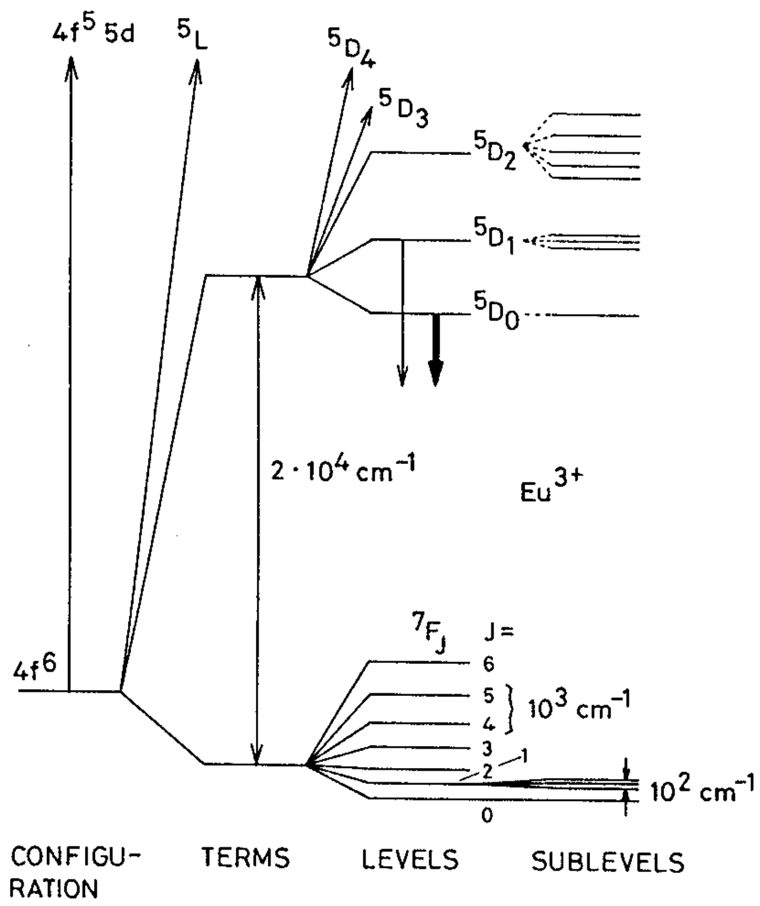
Energy level structure of trivalent lanthanide ions

- Partly filled 4f shell – multiple configurations

  Eu^{3+} $4f^6$ $\rightarrow$ 6 electrons for 7 f-orbitials (2 possible spin orientations)
  14!/(6!(14-6)!) = 3003 different arrangments
- 4f shell well shielded from the environment by closed $5s^2$ and $5p^6$ shells
- Energy level splitting due to:
  - Electrostatic interactions
  - Spin-orbit coupling
  - Crystal-field (CF) interactions

Splitting of $4f^6$ levels of Eu^{3+}



Ref. J.C.G. Bünzli, Inorg. Chim. Acta 139 (1987) 2019.

Free-ion levels of Eu^{3+}

$^{2S+1}L_J$	Energy (/cm^{-1})
$^7F_0$	0
$^7F_1$	379
$^7F_2$	1043
$^7F_3$	1896
$^7F_4$	2869
$^7F_5$	3912
$^7F_6$	4992
$^5D_0$	17227
$^5D_1$	18973
$^5D_2$	21445
$^5D_3$	24335
$^5L_6$	25125
$^5L_7$	26177
$^5G_2$	26269
$^5G_3$	26493
$^5G_4$	26611
$^5G_5$, $^5G_6$	26642
$^5L_8$	27095
$^5D_4$	27583
$^5L_9$	27844
$^5L_{10}$	28341
$^5H_3$	30870
$^5H_7$	31070
$^5H_4$	31292
$^5H_6$, $^5H_5$	31511
$^3P_0$	32790
$^5F_2$	33055
$^5F_3$	33092
$^5F_1$	33366
$^5F_4$	33513
$^5F_5$	34040
$^5I_4$	34057
$^5I_5$	34388
$^5I_6$	34966
$^5I_7$	35429
$^5I_8$	35453
$^5K_5$	36168
$^5K_6$	37320
$^3P_1$	38132
$^5K_7$	38247
$^5G_2$	38616
$^5K_8$	38667
$^3K_6$, $^3I_6$	38780

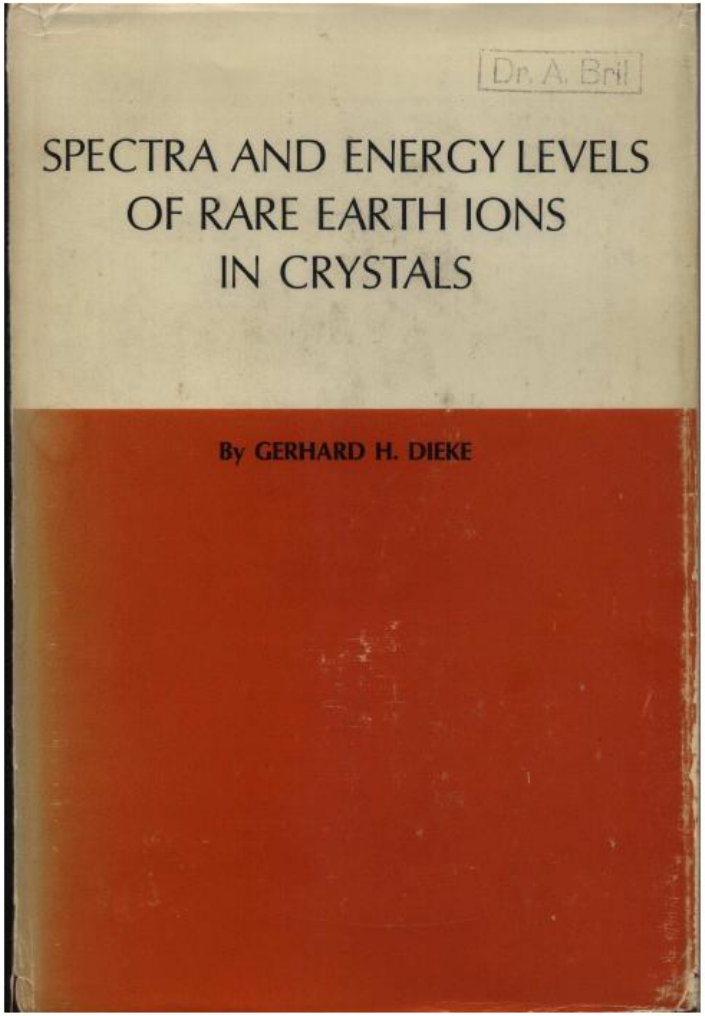
Ref. : K. Binnemans, Bull. Soc. Chim. Belg. 105 (1996) 793.

Number of levels

$$\frac{(4\ell+2)!}{N!(4\ell+2-N)!} = \frac{14!}{N!(14-N)!}$$

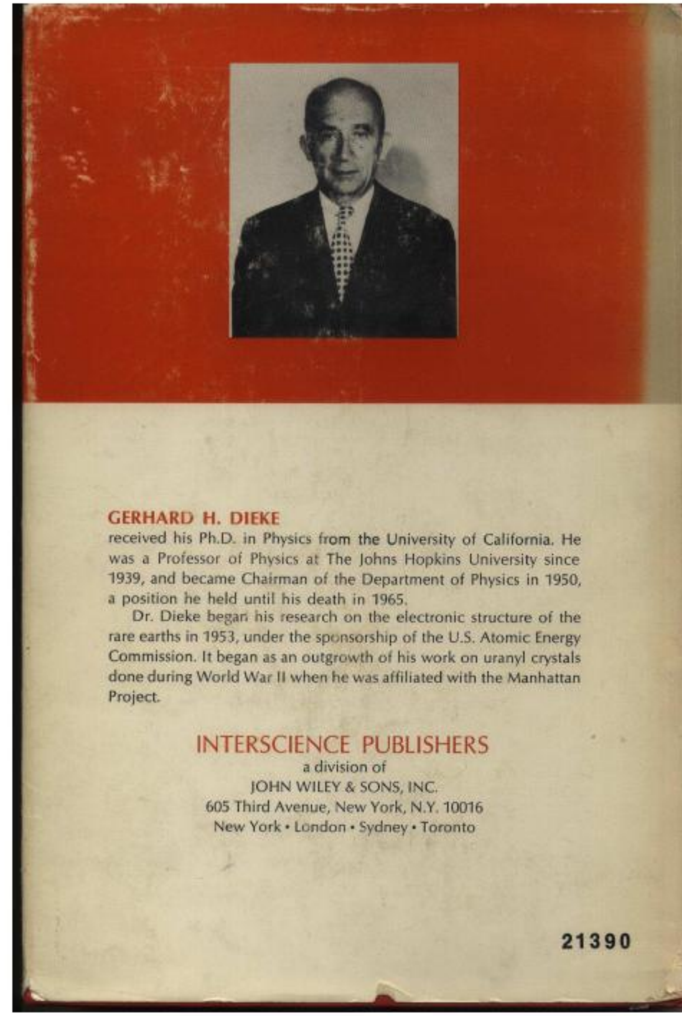
Number of f electrons	Number of terms ^{2S+1}L	Number of levels $^{2S+1}L_J$	Number of LF sublevels $^{2S+1}G_x$
1 13	1	2	14
2 12	7	13	91
3 11	17	41	364
4 10	47	107	1001
5 9	73	198	2002
6 8	119	295	3003
7	119	327	3432

Dieke (1968)



SPECTRA AND ENERGY LEVELS OF RARE EARTH IONS IN CRYSTALS

By GERHARD H. DIEKE


GERHARD H. DIEKE
received his Ph.D. in Physics from the University of California. He was a Professor of Physics at The Johns Hopkins University since 1939, and became Chairman of the Department of Physics in 1950, a position he held until his death in 1965.

Dr. Dieke began his research on the electronic structure of the rare earths in 1953, under the sponsorship of the U.S. Atomic Energy Commission. It began as an outgrowth of his work on uranyl crystals done during World War II when he was affiliated with the Manhattan Project.

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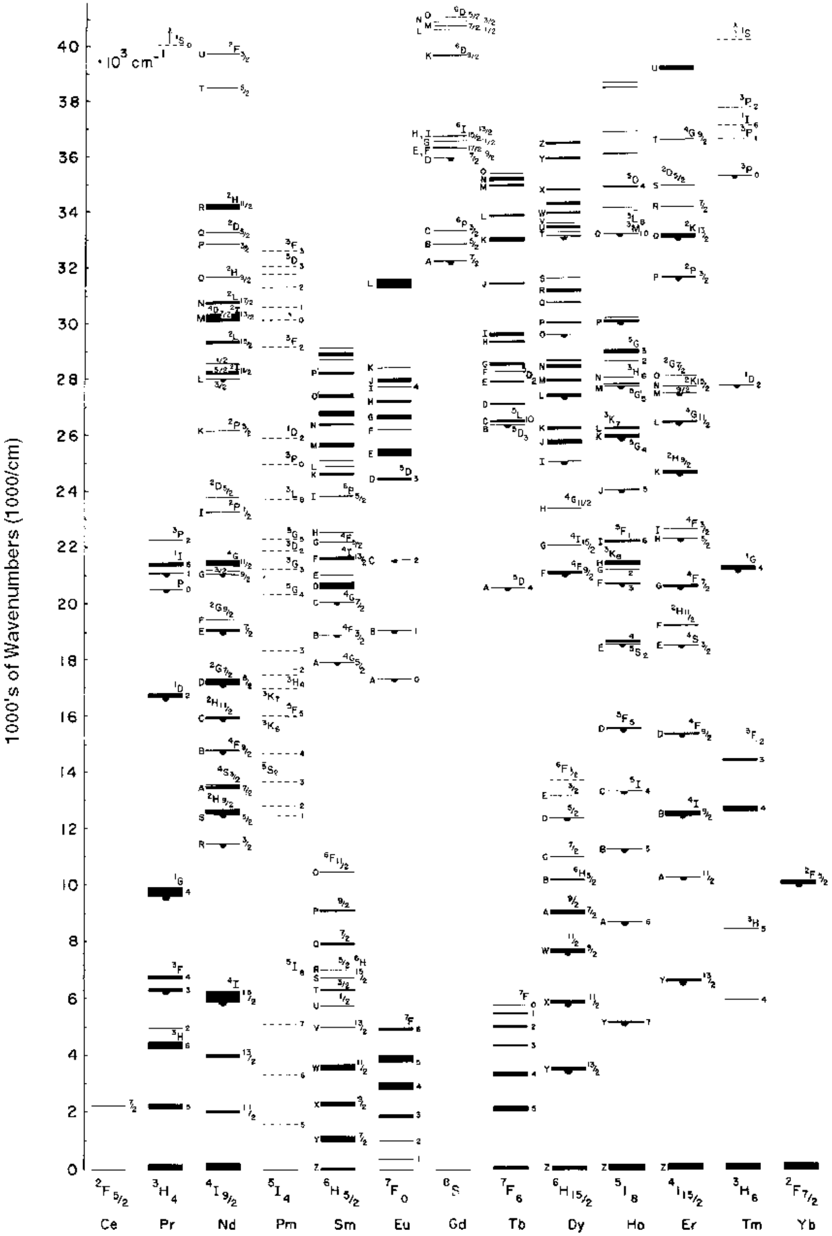
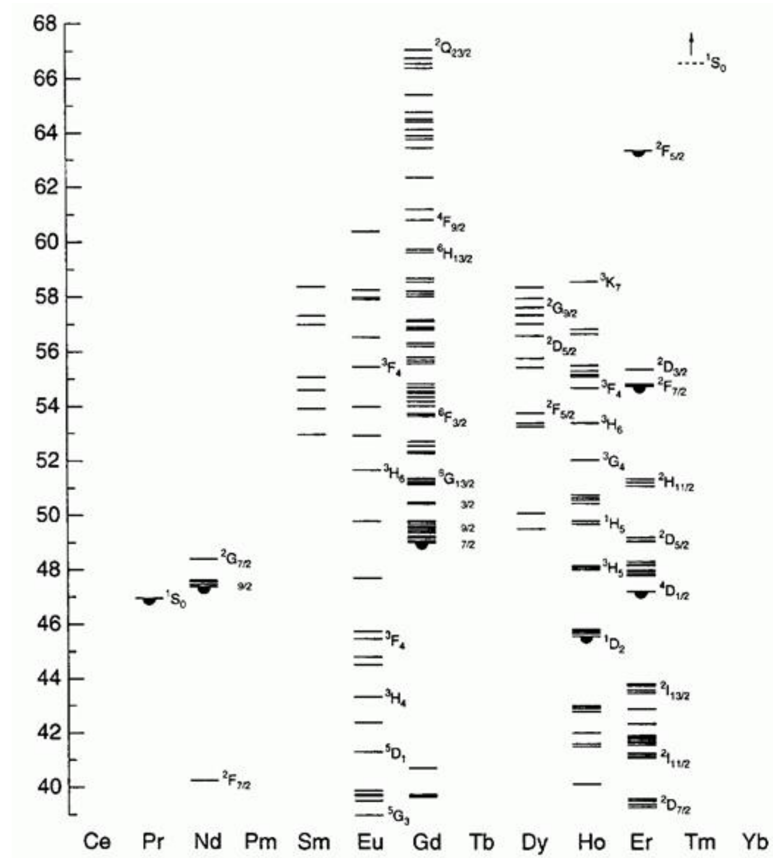
Classic 'Dieke Diagram' for Rare Earth Ions



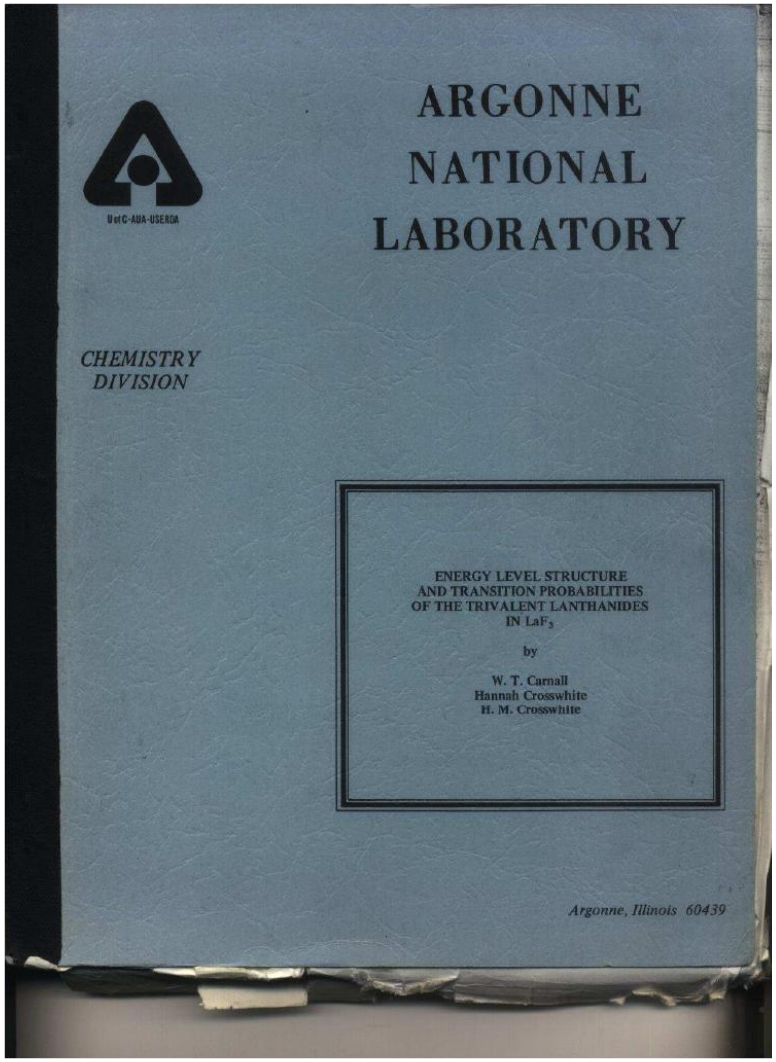
G. H. Dieke. Spectra and energy levels of rare earth ions in crystals (Interscience Publishers. New York. 1968)

Extension to VUV



Ref.: R.T Wegh et al. J. Lumin. 66-68 (2000) 1002.

ANL report – Carnall, Crosswhite & Crosswhite energy levels in LaF_3 - 1977



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APPENDIX VIII

TABLE 1
GD+3:LAF3

OBSERVED	CALC	O-C	STATE	J	MJ
0.0	1	0	8S	7/2	-7/2
0.0	1	0	8S	7/2	5/2
0.0	1	0	8S	7/2	3/2
0.0	1	0	8S	7/2	1/2
32177.11	32183	-5	6P	7/2	-7/2
32185.62	32189	-3	6P	7/2	5/2
32199.61	32209	-8	6P	7/2	3/2
32228.57	32232	-3	6P	7/2	1/2
32771.75	32787	-14	6P	5/2	3/2
32791.96	32788	4	6P	5/2	5/2
32809.29	32799	10	6P	5/2	1/2
33352.00	33351	1	6P	3/2	1/2
33370.00	33366	4	6P	3/2	3/2
35923.00	35929	-5	6I	7/2	5/2
35945.24	35939	6	6I	7/2	3/2
35969.03	35962	7	6I	7/2	-7/2
35996.14	35979	17	6I	7/2	1/2
36275.25	36268	8	6I	9/2	5/2
36286.08	36276	10	6I	9/2	-7/2
36306.24	36297	9	6I	9/2	3/2
36314.26	36305	10	6I	9/2	-9/2
36333.45	36316	17	6I	9/2	1/2
36340.81	36342	-1	6I	17/2	-9/2
36343.03	36344	0	6I	17/2	-11/2
36347.18	36344	3	6I	17/2	-7/2
36351.69	36346	5	6I	17/2	13/2
36354.80	36348	7	6I	17/2	15/2
36364.51	36350	15	6I	17/2	5/2
36371.71	36355	17	6I	17/2	3/2
36377.86	36358	20	6I	17/2	17/2
36384.90	36359	26	6I	17/2	1/2
36551.43	36556	-4	6I	11/2	-7/2
36563.33	36567	-3	6I	11/2	-9/2
36573.18	36575	-1	6I	11/2	5/2
36586.14	36593	-6	6I	11/2	3/2
36594.86	36593	2	6I	11/2	-11/2
36613.04	36611	2	6I	11/2	1/2
36661.81	36674	-11	6I	15/2	-9/2
36670.99	36686	-14	6I	15/2	-11/2
36679.98	36690	-9	6I	15/2	-7/2
36690.17	36706	-14	6I	15/2	5/2
36700.50	36707	-5	6I	15/2	13/2

Types of transitions

- f-f transitions
- f-d transitions
- charge-transfer (CT) transitions

f-f transitions

- Narrow bands
- Weak intensities: $\varepsilon < 10\ M^{-1}cm^{-1}$
- Barycenters of CF sublevels are not much dependent on the nature of the Ln^{3+} environment; therefore energy of the transitions is more or less constant
  (but not CF splitting!)
- Electric dipole transitions (ED) are forbidden
  Magnetic dipole (MD) transitions are allowed, but very weak
- Number of components for a given ${}^{(2S'+1)}L'_{J'} \leftarrow {}^{2S+1)}L_J$ transition depends on the site symmetry
- Some transitions are **hypersensitive**, i.e. very sensitive to small changes in the Ln^{3+} environment.

Selection rules for f-f transitions

Electric dipole transitions

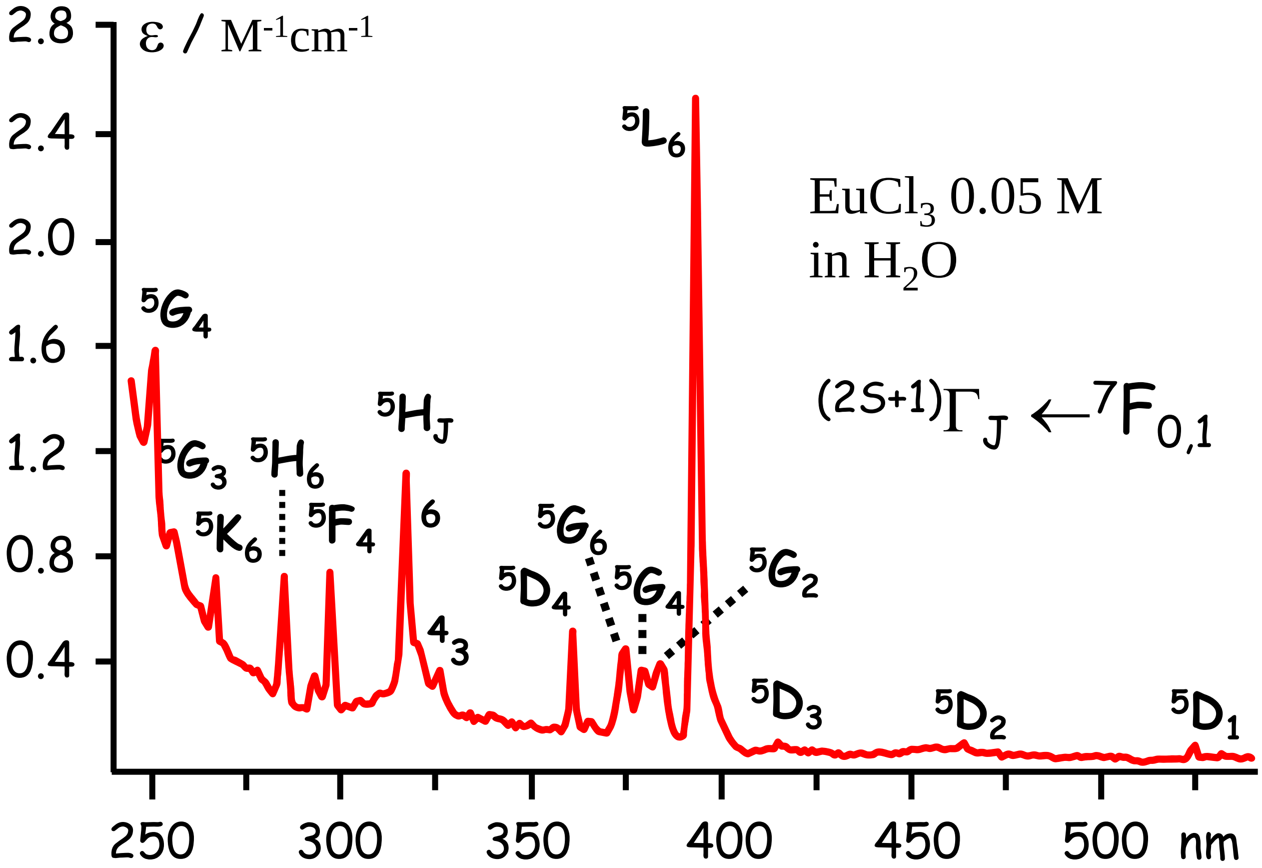
$\Delta l = \pm 1$ Laporte's rule
$\Delta S = 0$ spin rule
$\Delta L \le 6$ 0, 2, 4, 6
$\Delta L \le 6$ 0, 2, 4, 6

Relaxed by J-mixing

Magnetic dipole transitions

$\Delta l = 0$
$\Delta S = 0$
$\Delta L = 0$
$\Delta J = 0, \pm 1$, except 0-0

Typical absorption spectrum of Eu^{3+}

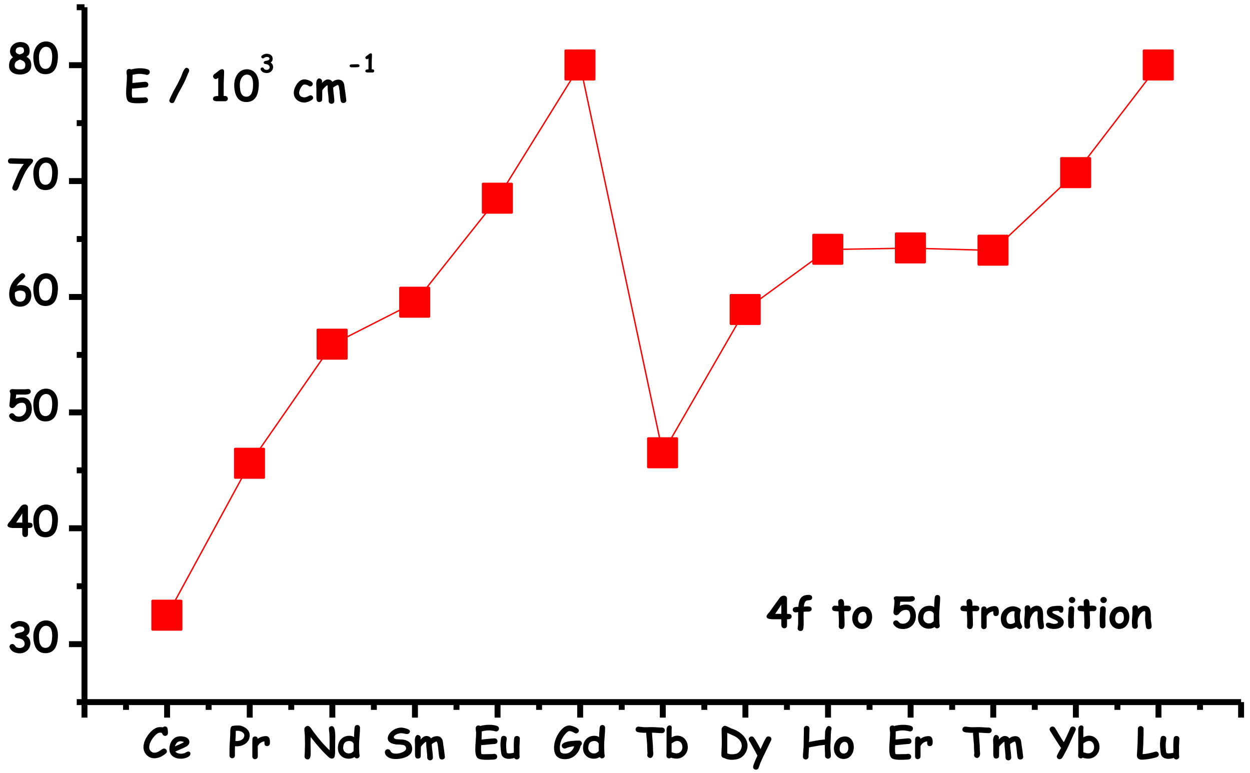


Ref. : J.C.G Bünzli, Lanthanide course

f-d transitions

Allowed by Laporte's rule, ≈ 100-1000 $M^{-1}cm^{-1}$

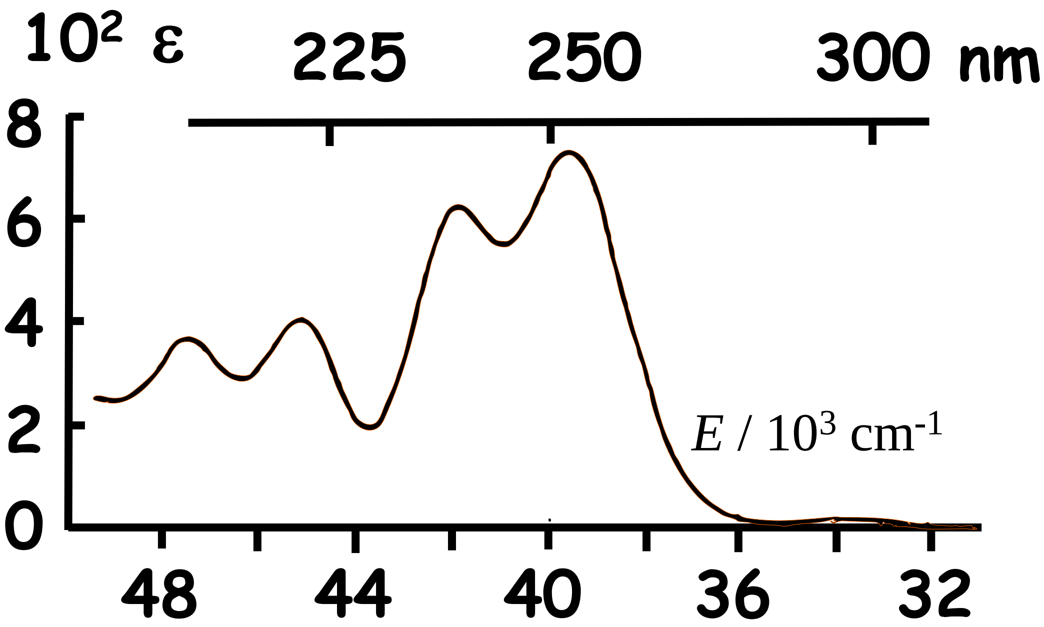
Highly energetic, except for Ce^{3+}, Pr^{3+}, and Tb^{3+}

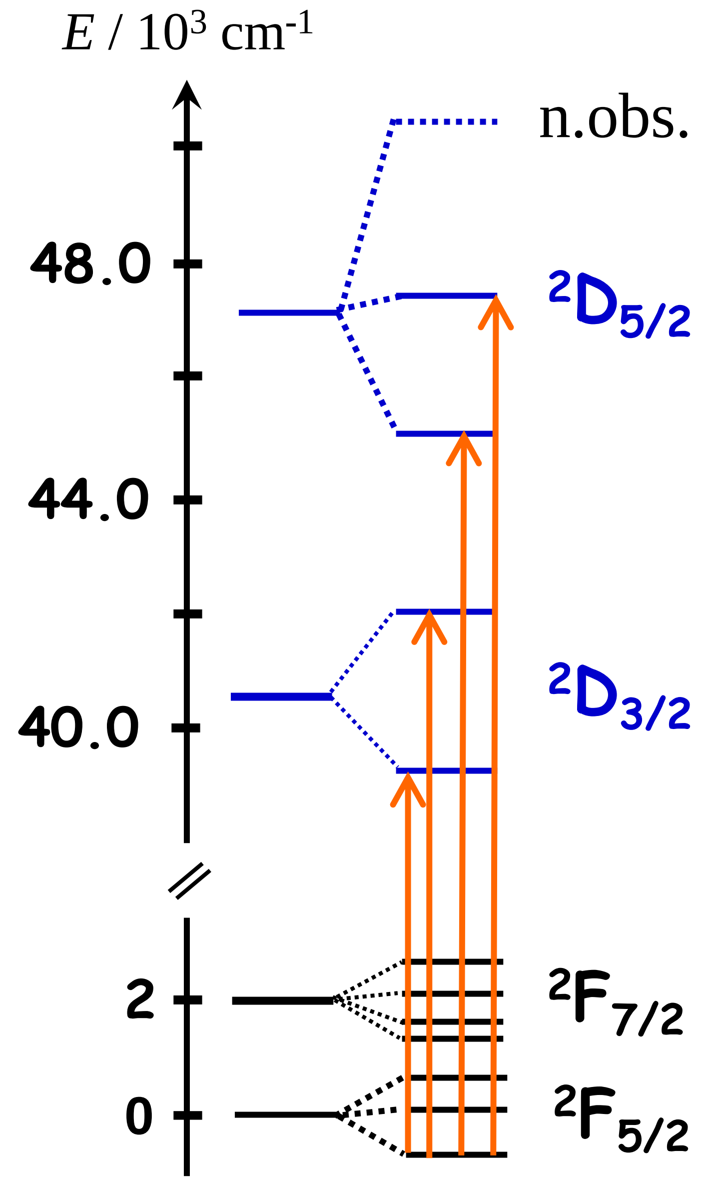


Ref. : J.C.G Bünzli, Lanthanide course

f-d transitions

$[Ce(H_2O)_9]^{3+}$, D_{3h} symmetry





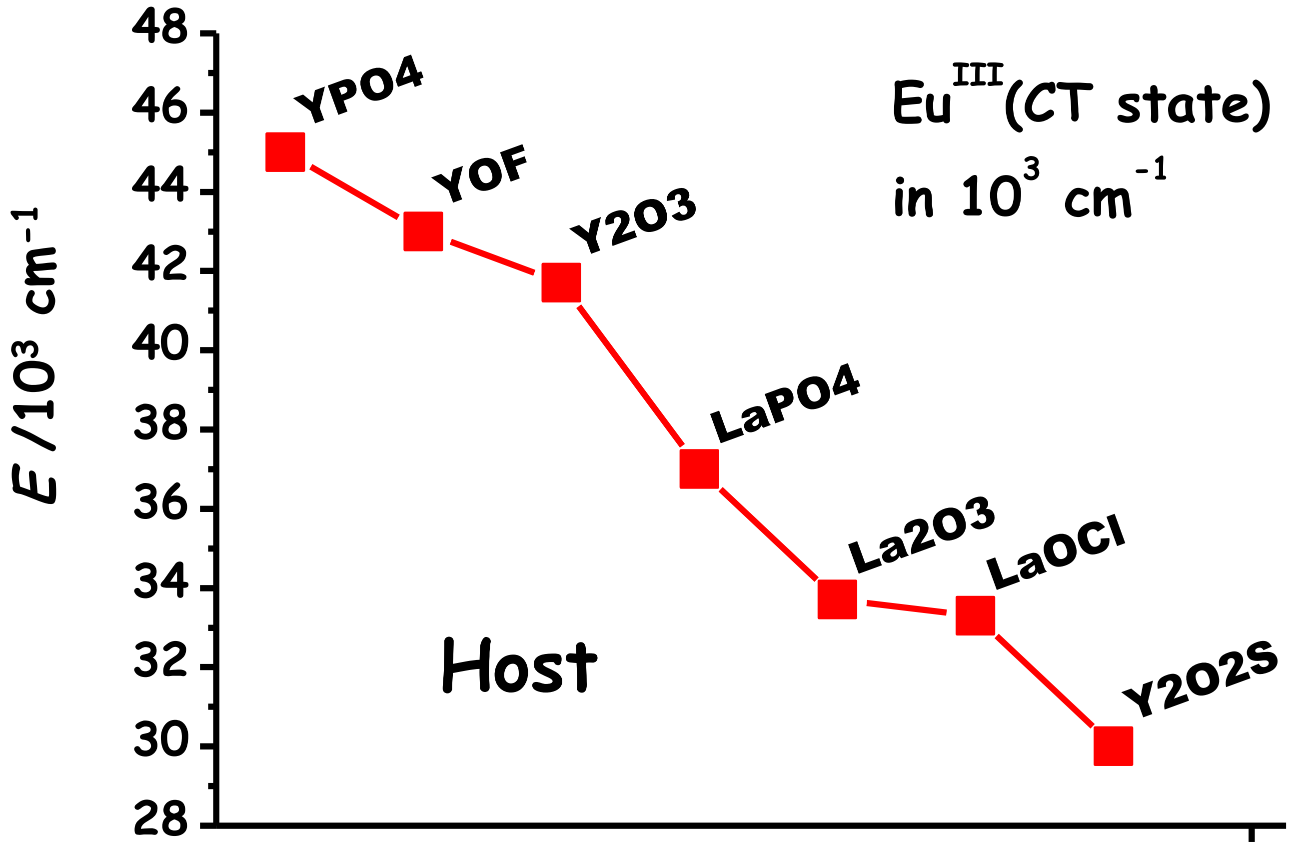
Ce^{3+} [Xe]$5d^1$ generates two levels, $^2D_{3/2}$ and $^2D_{5/2}$

Ref. : J.C.G Bünzli, Lanthanide course

Charge-transfer (CT) transitions

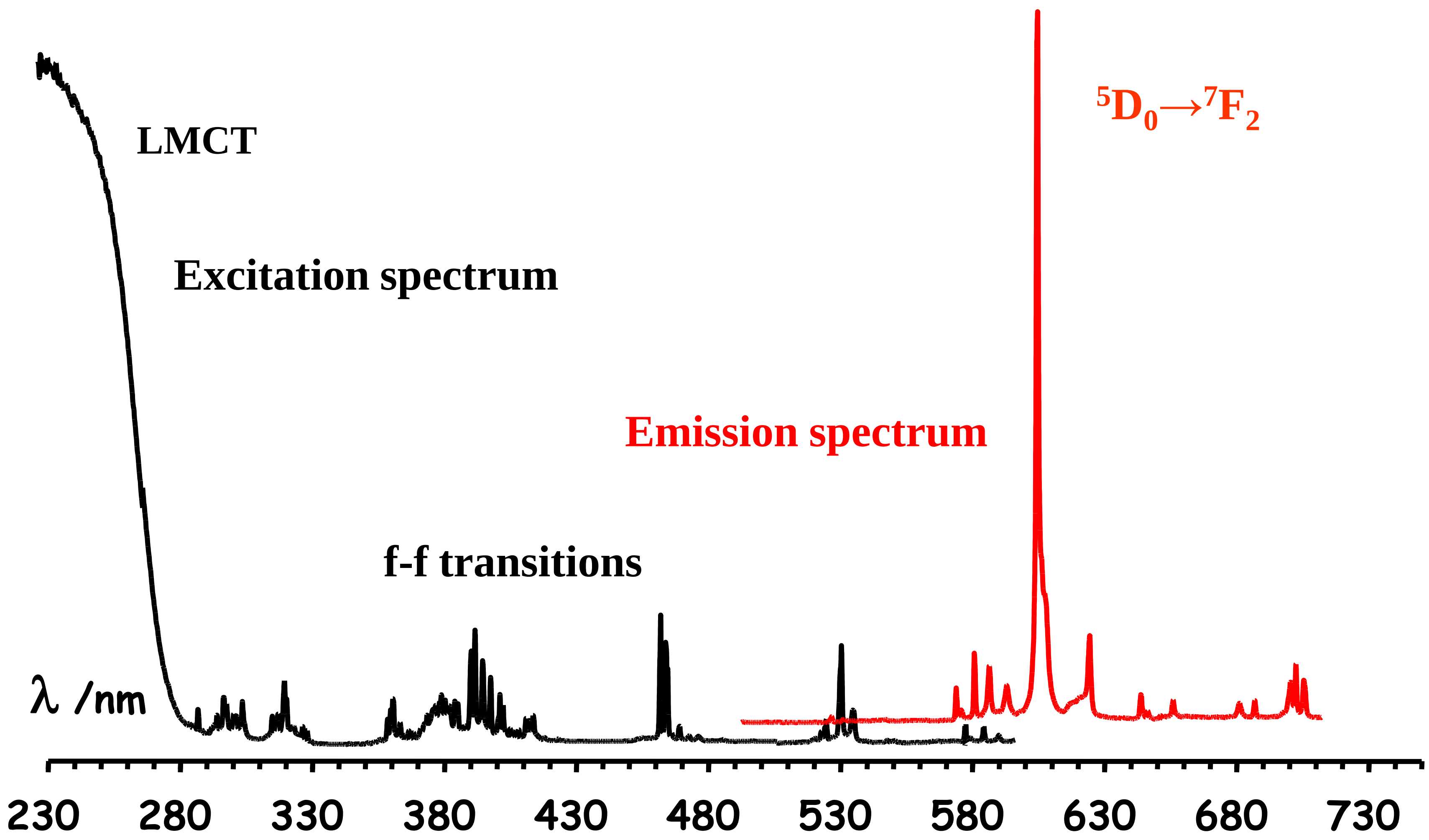
Allowed by Laporte's rule, » 200-500 $M^{-1}cm^{-1}$

Voor Eu^{3+}: LMCT (formal reduction to Eu^{2+})



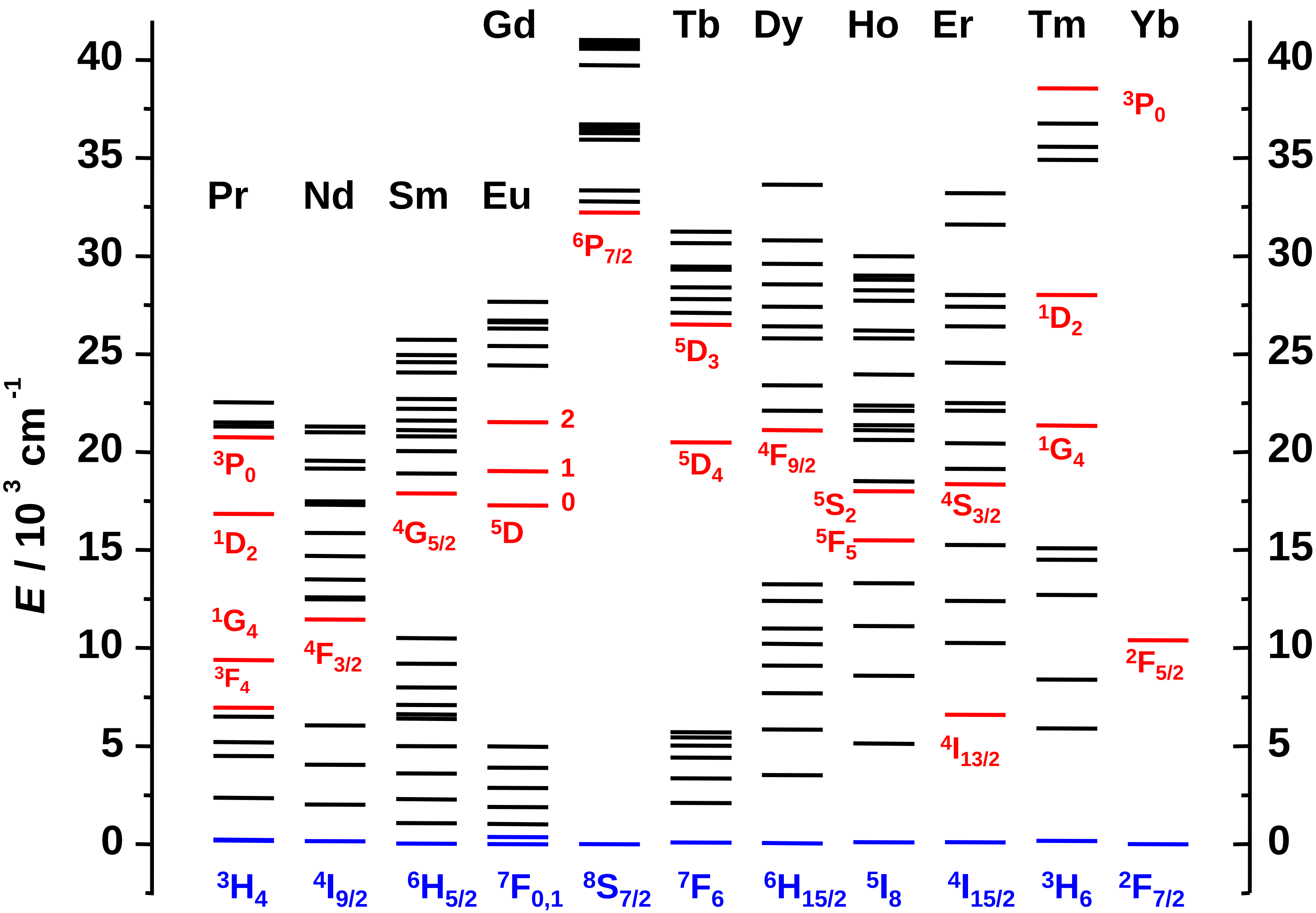
Ref. : J.C.G Bünzli, Lanthanide course

Red phosphor $Y_2O_3:Eu^{3+}$



Ref. : J.C.G Bünzli, Lanthanide course

4f emission spectra



Ref. : J.C.G Bünzli, Lanthanide course

Characteristic of lanthanide luminescence

- Narrow emission lines (high chromatographic purity)
- Every spectroscopically active lanthanide ion has a typical luminescence color
- Emission color is not very dependent on ion's environment
- Large Stokes shift
- Long-lives excited states (several ms in inorganic matrices)
- Direct excitation in 4f-levels is not efficient
  Sensitized luminescence is preferred

Energy gap law

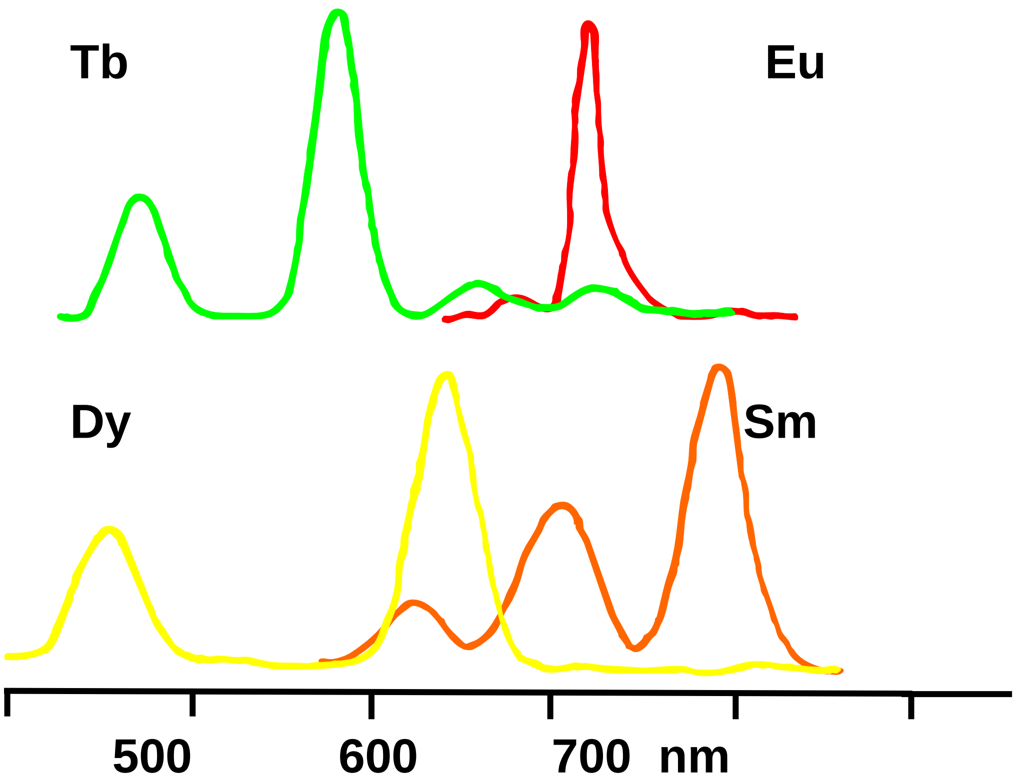
- The larger the gap between the excited state and the more energetic component of the ground state multiplet, the more intense the luminescence
  (less non-radiative deactivation).

Gd 32100 cm^{-1}	Yb 10400 cm^{-1}	Tm 6200 cm^{-1}
Tb 14800 cm^{-1}	Dy 7800 cm^{-1}	Er 5900 cm^{-1}
Eu 12300 cm^{-1}	Sm 7400 cm^{-1}	Nd 4400 cm^{-1}

- Gd^{3+} is the best emitter, but the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition occurs in the UV (around 310 nm).
- Eu^{3+}, Tb^{3+} have often large intrinsic quantum yields and are used as luminescent probes.

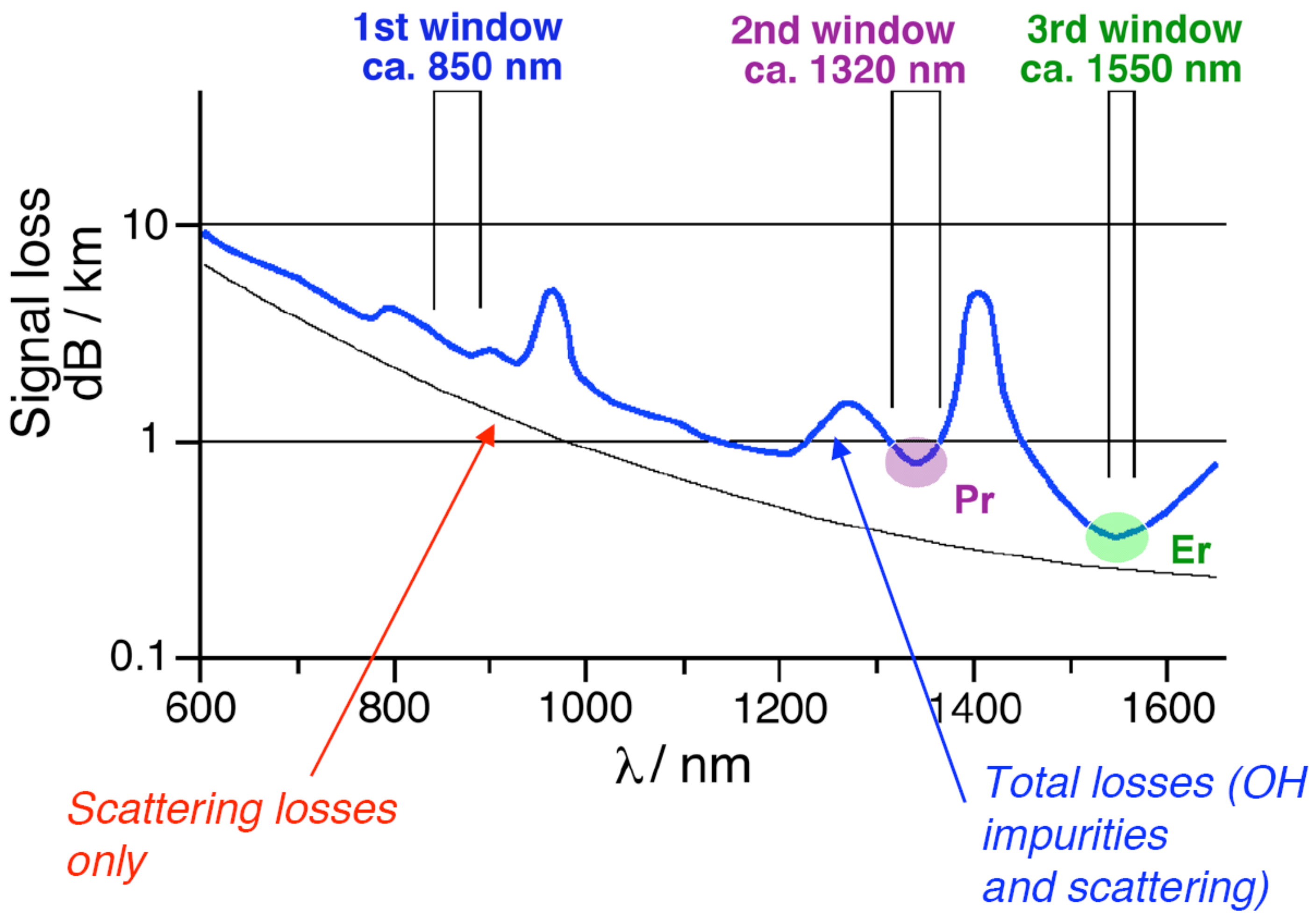
Luminescence of lanthanide ions

Visible luminescence observed for Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}



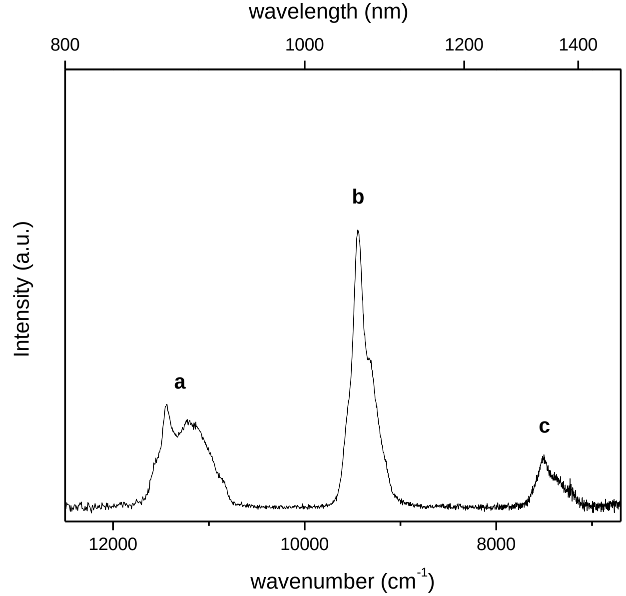
Pr^{3+} (1.33 mm), Nd^{3+} (1.06 mm), Er^{3+} (1.54 mm), and Yb^{3+} (0.98 mm) have interesting emission bands in the NIR range, some of them are in the telecommunication window (1 – 1.6 mm)

NIR luminescence: telecommunication window

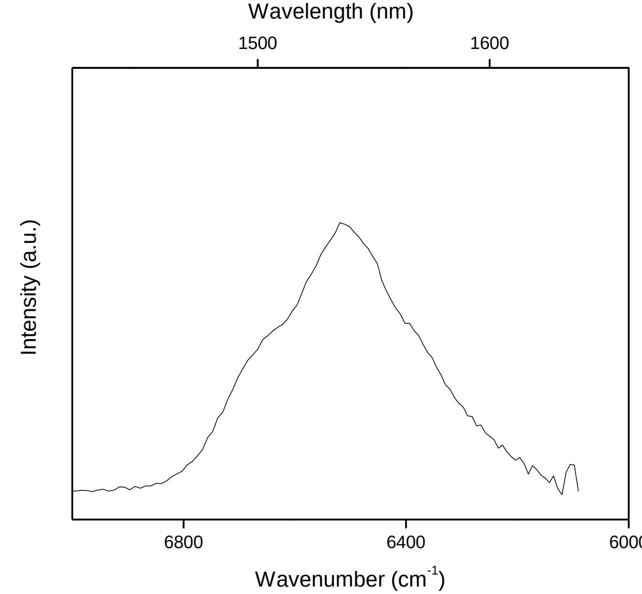


NIR luminescence

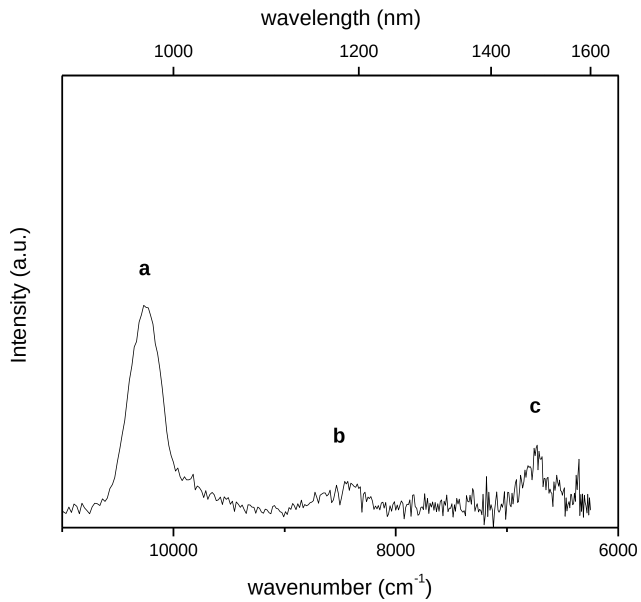
Nd^{3+}



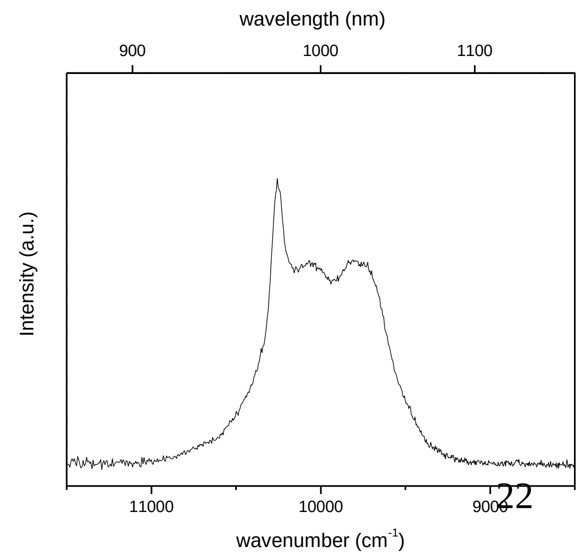
Er^{3+}



Ho^{3+}



Yb^{3+}



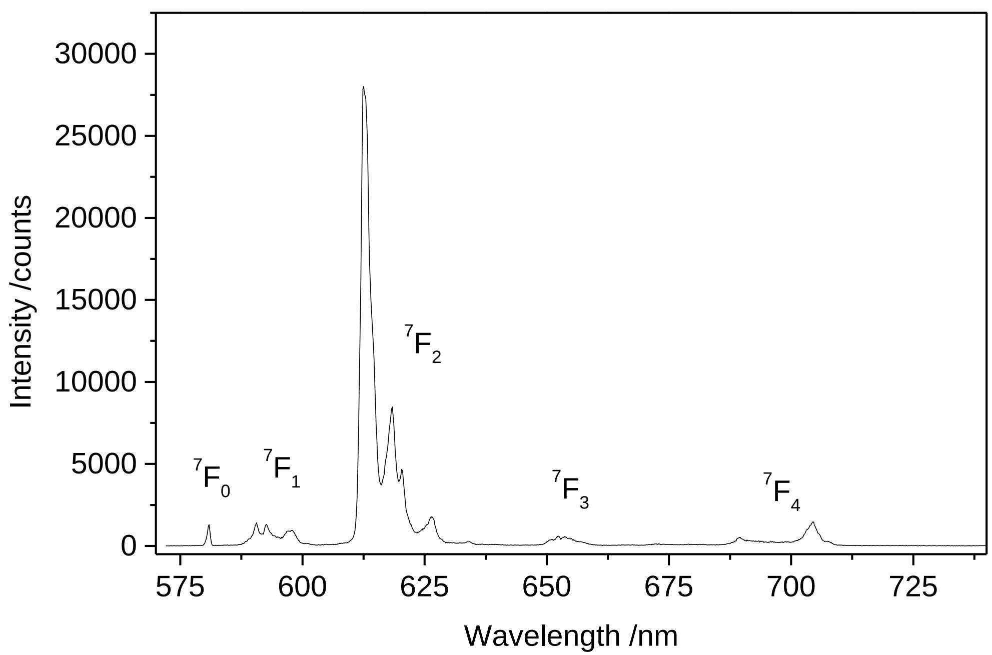
Transitions in europium(III) luminescence spectra

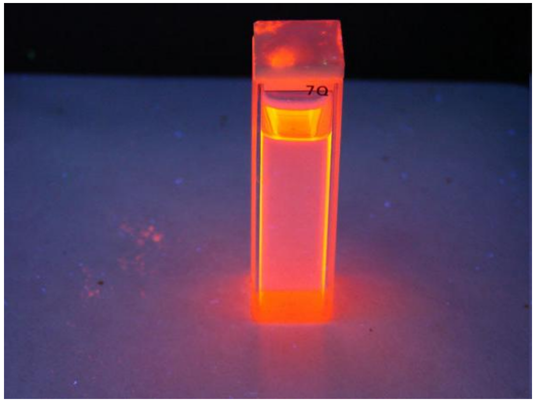
Transitions with $\Delta J = 0, 2$ are hypersensitive, i.e. very sensitive to minute changes in the environment of metal ion

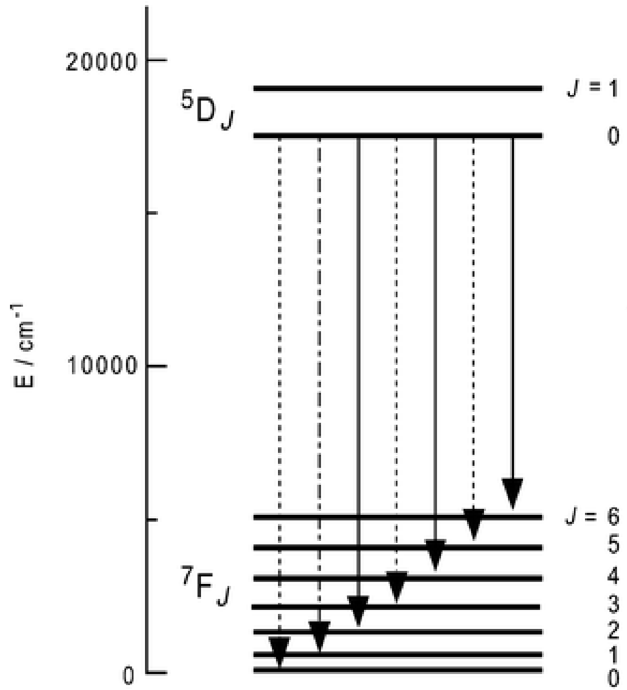
Transitions from $^5D_0$ to ^7F_J for J =

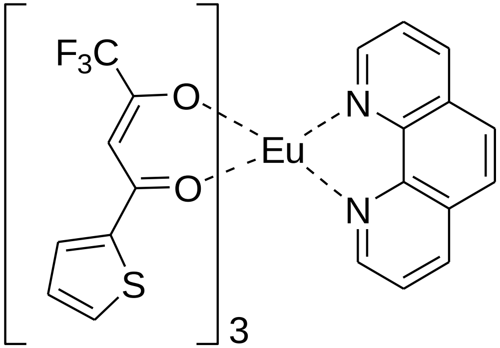
0	ED	577-581 nm	non-degenerate, highly forbidden allowed in some symmetries
1	MD	585-600 nm	allowed, weak intensity almost independent from environment
2	ED	610-625 nm	hypersensitive, forbidden if inversion centre *i* is present
3	ED	640-655 nm	forbidden, very weak
4	ED	680-710 nm	allowed (except if *i*)
5	ED	740-770 nm	forbidden, very weak
6	ED	810-840 nm	allowed, weak (except if *i*)

Luminescence of [Eu(tta)$_3$(phen)]

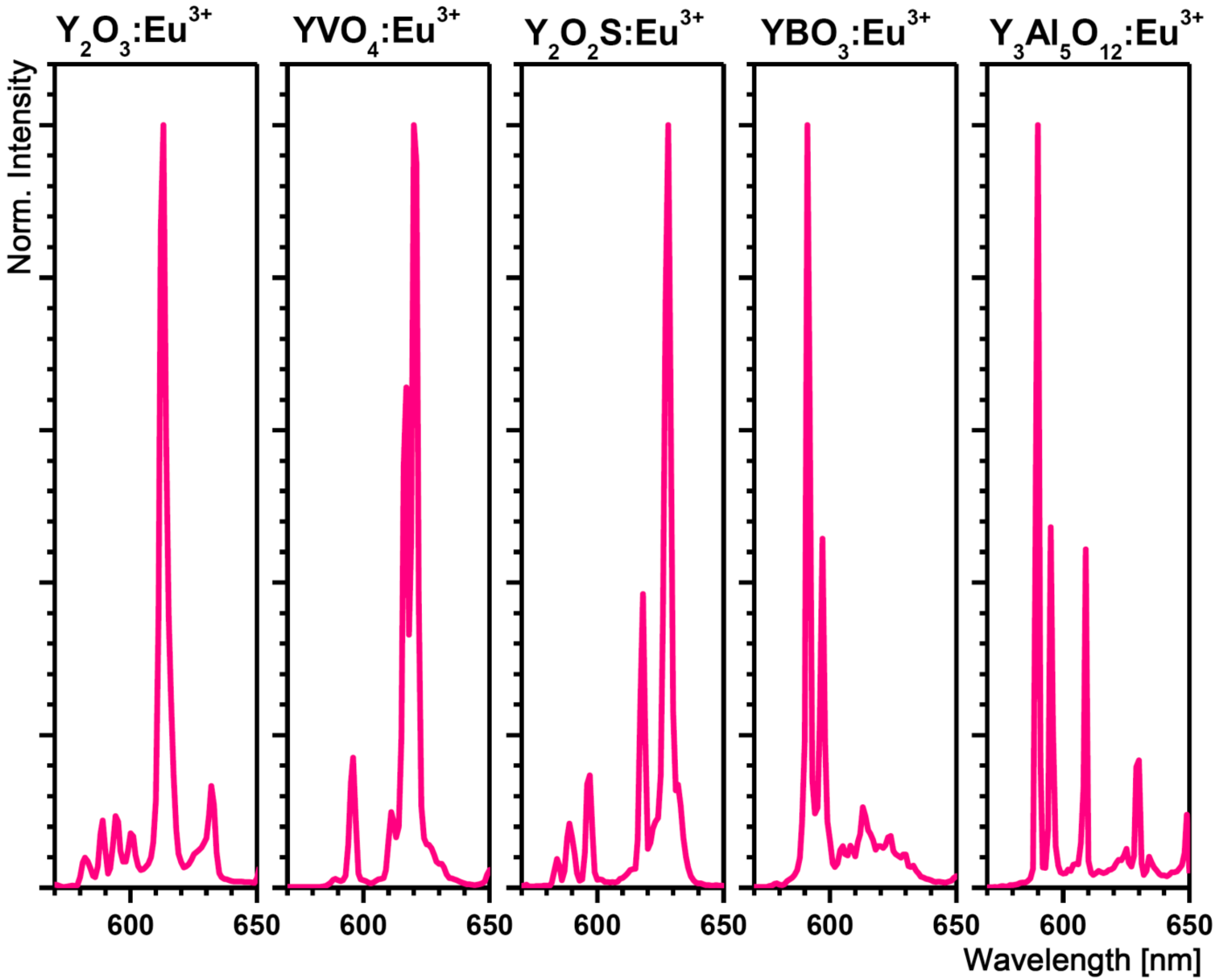






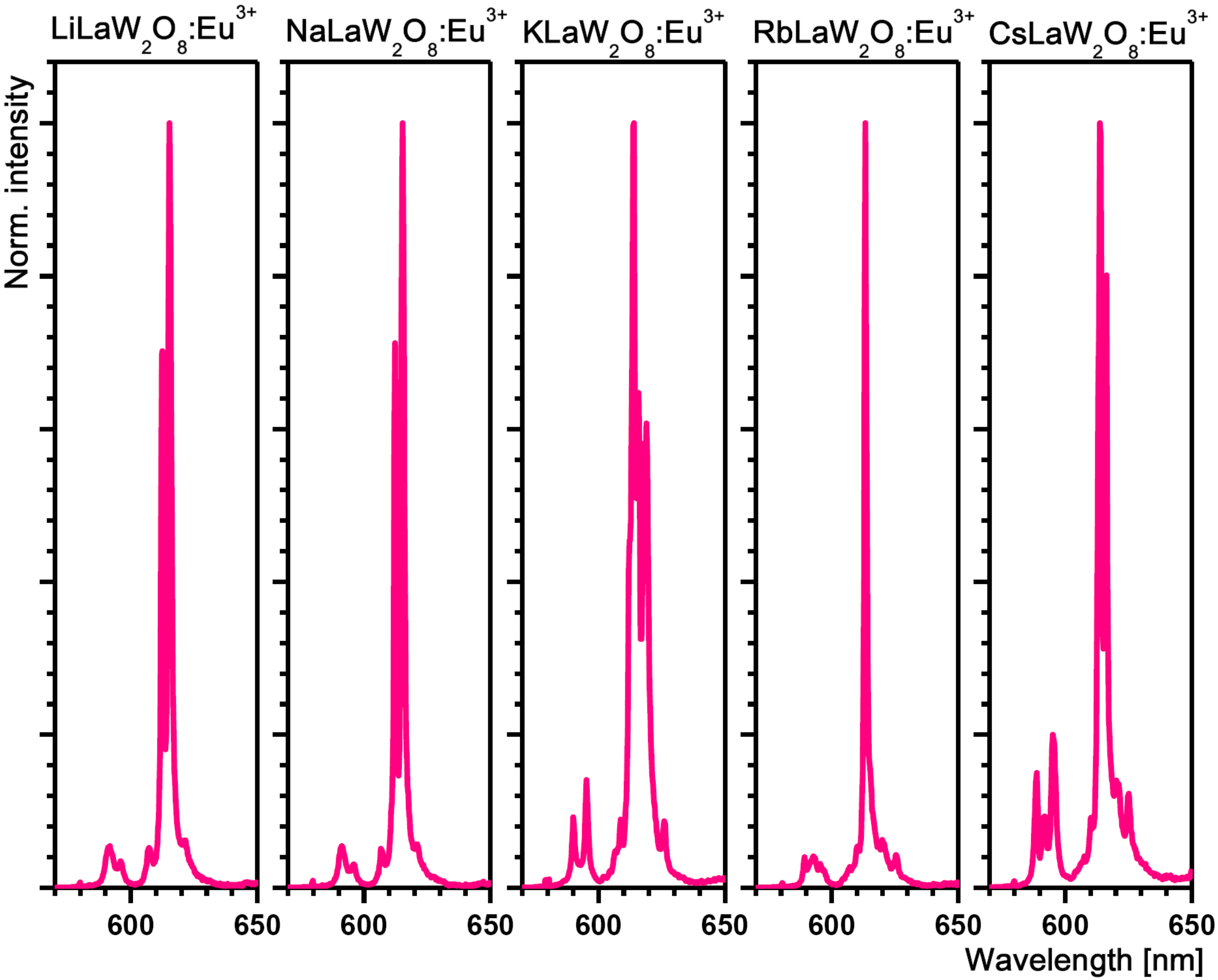


Europium spectra



Source: Tailorlux GmbH

Europium spectra



Source: Tailorlux GmbH

$SnO_2:Eu^{3+}$– centrosymmetric compound (D_{2h})

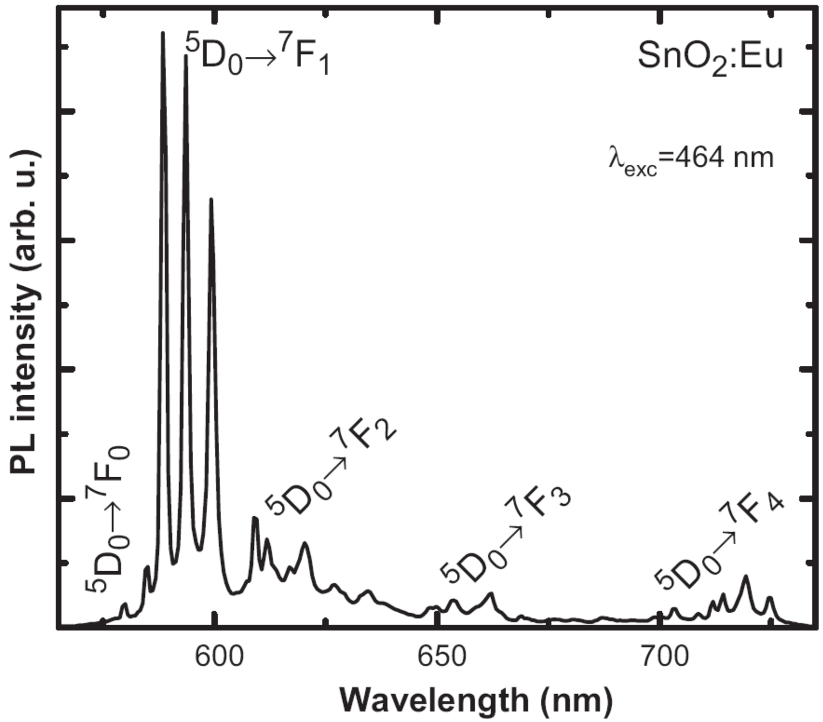


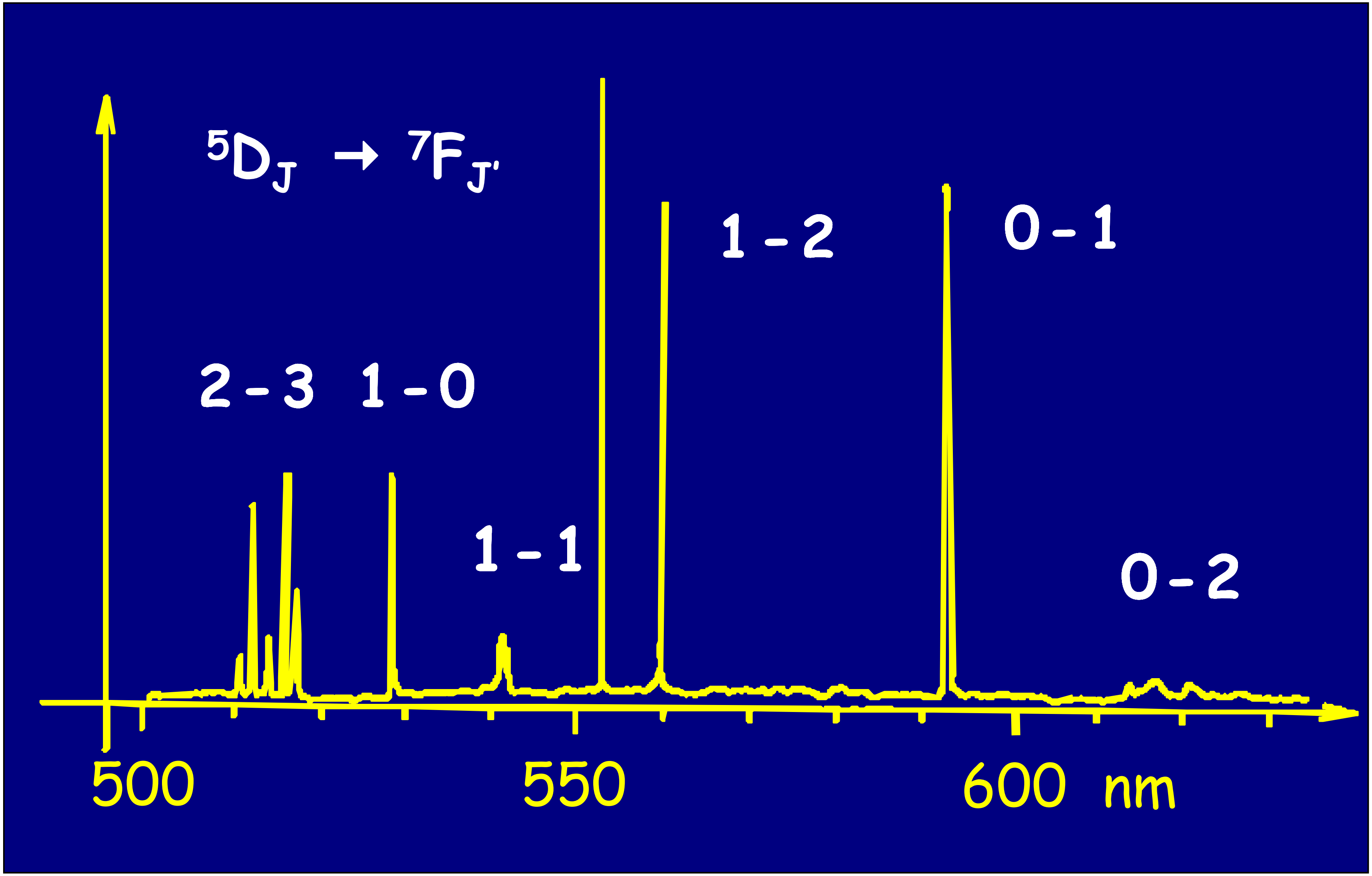
Fig. 3. Photoluminescence spectrum of sol–gel-prepared SnO_2:Eu powder excited at 464 nm and measured at room temperature. The spectrum is corrected to instrumental response.

Ref.: M. Ma et al. J. Alloys Compds. 509 (2011) 3441

Other excited states

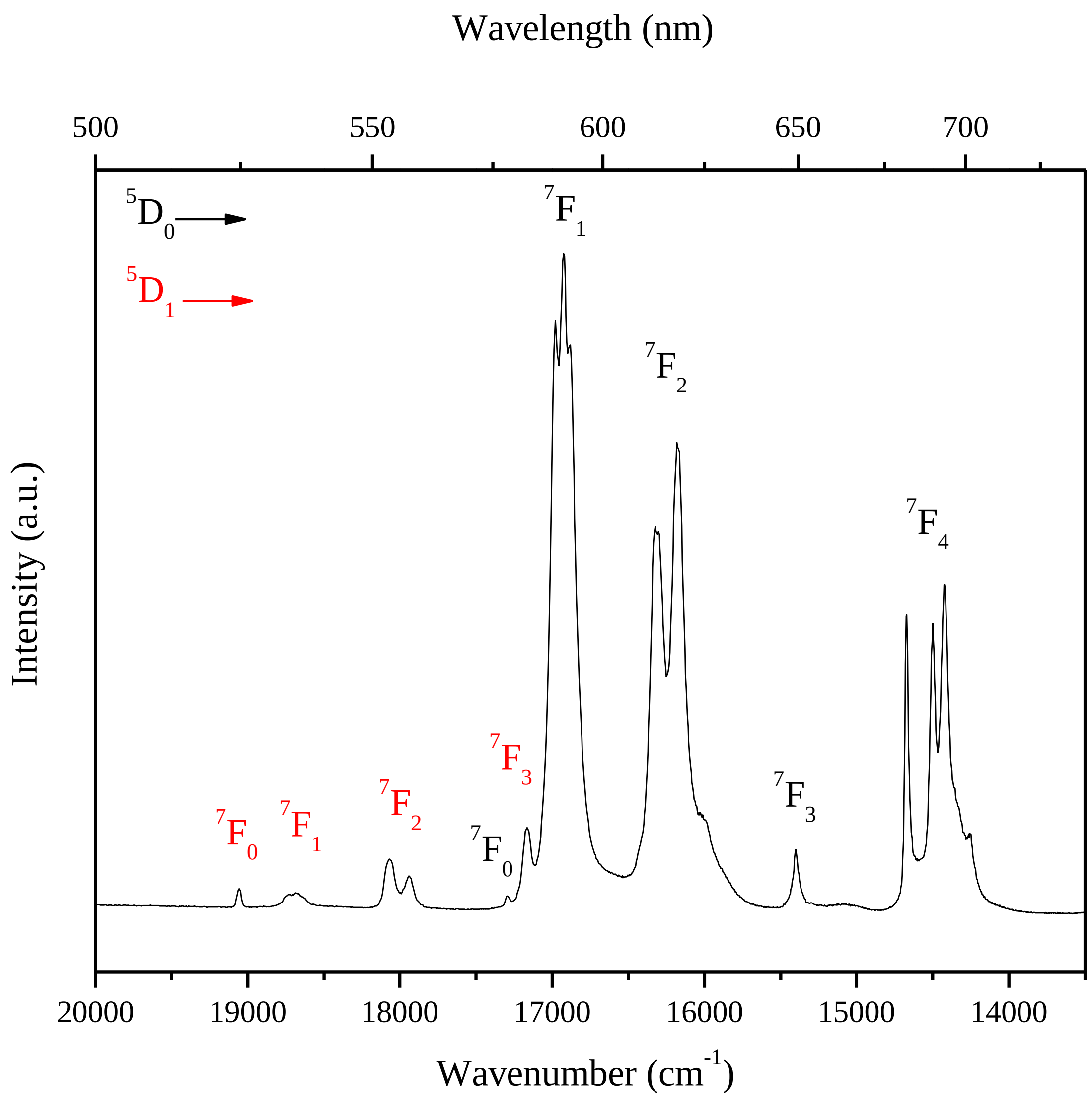
- Most transitions in Eu^{3+} luminescence spectra start from $^5D_0$
- In inorganic matrices, transitions from $^5D_1$ and $^5D_2$ are possible
- Transitions from $^5D_3$ are very rare
- In molecular compounds, often only transitions from $^5D_0$ are observed, because of stronger radiationless deactivation.
- In spectra with luminescence from $^5D_1$ and $^5D_2$, there can be an overlap between the $^5D_0 \rightarrow {}^7F_J$ and the $^5D_{1,2} \rightarrow {}^7F_J$ lines.

Luminescence of $Cs_2Na(Y:Eu)Cl_6$ (Elpasolite): O_h



Ref. : J.C.G Bünzli, Lanthanide course

$LaF_3:Eu^{3+}$



Ref.: K. Lunstroot et al., J. Phys. Chem. C 113 (2009) 13532.

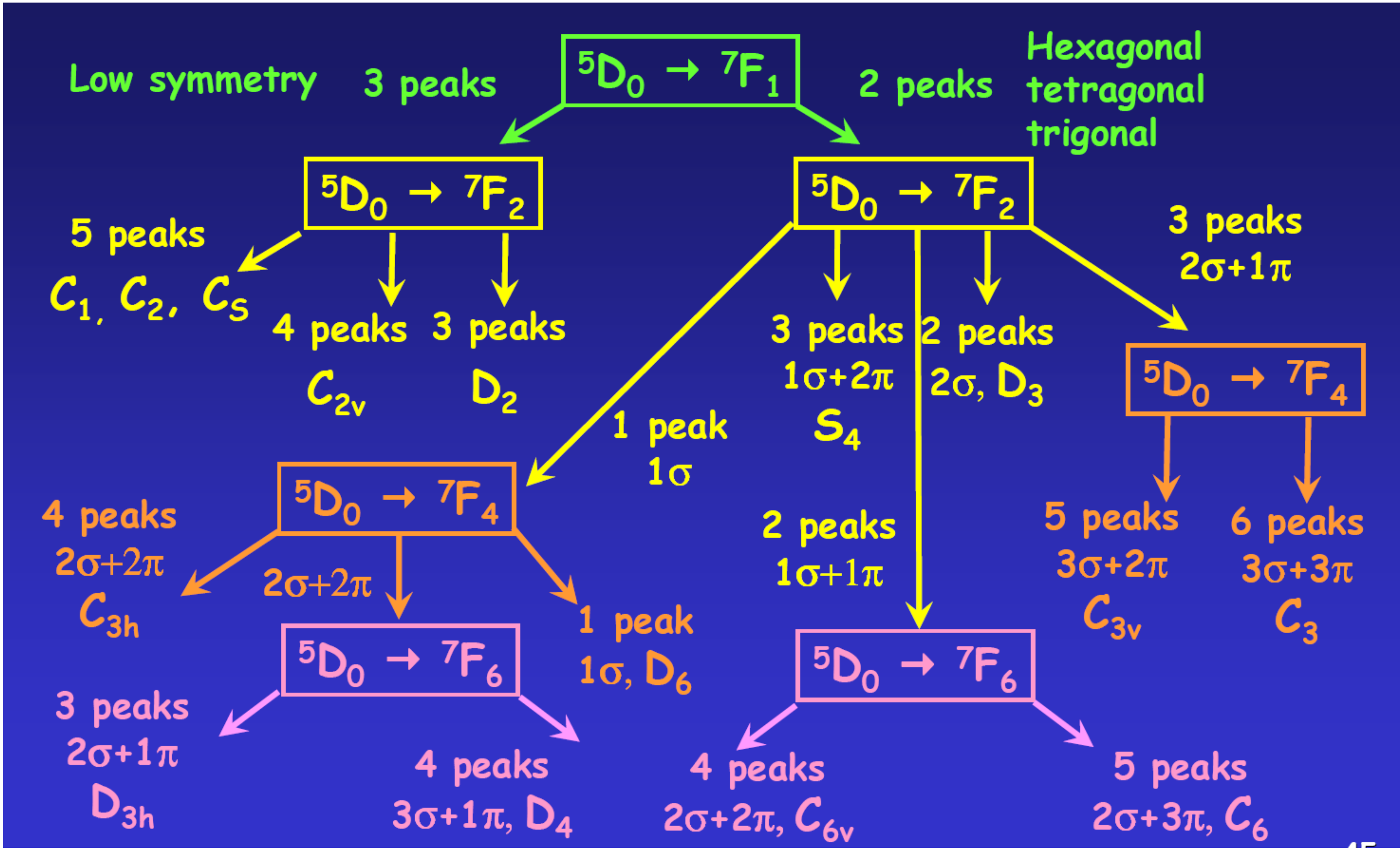
Number of emission lines for Eu^{3+} in different symmetries

Table 4 Number of emission bands from $^5D_0$ to ^7F_J (J = 0–4) for Eu^{3+} at certain point symmetry sites[a]

Point group	Example[b]	Terminal state					Point Group	Example	Terminal state				
		$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$			$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$
C_1	$BiEuGeO_5$	1	3	5	7	9	C_{4h}		0	2	0	0	0
C_s	$YOOH:Eu^{3+}$	1	3	5	7	9	C_{4v}	$GdOCl:Eu^{3+}$	1	2	2	2	4
C_2	$LaF_3:Eu^{3+}$	1	3	5	7	9	D_{4h}		0	2	0	0	0
C_{2v}	$Eu(CH_3SO_3)_3$	1	3	4	5	7	D_{4d}		0	2	0	1	2
C_i	$YBO_3:Eu^{3+}$	0	3	0	0	0	S_4	$LiYF_4:Eu^{3+}$	0	2	3	4	4
C_{2h}		0	3	0	0	0	D_4	$LiEuCl_4$	0	2	1	3	3
D_2	$Y_3Al_5O_{12}:Eu^{3+}$	0	3	3	6	6	C_6		1	2	2	2	2
D_{2h}		0	3	0	0	0	C_{6v}		1	2	2	2	2
D_{2d}	$YVO_4:Eu^{3+}$	0	2	2	3	3	D_6		0	2	1	2	1
D_3	$Na_3[Eu(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$	0	2	2	4	4	C_{6h}		0	2	0	0	0
C_3	$Mg_3Eu_2(NO_3)_{12}\cdot 24H_2O$	1	2	3	5	6	D_{6h}		0	2	0	0	0
C_{3v}	$Y_2O_2S:Eu^{3+}$	1	2	3	3	5	T		0	1	1	2	2
C_{3h}	$Eu(C_2H_5SO_4)_3\cdot 9H_2O$	0	2	1	3	4	T_d		0	1	1	1	1
C_{3i}	$Y_2O_3:Eu^{3+}$	0	2	0	0	0	T_h	$Cs_2NaEu(NO_2)_6$	0	1	0	0	0
D_{3d}	$Eu_2Ti_2O_7$	0	2	0	0	0	O		0	1	0	1	1
D_{3h}	$Eu(BrO_3)_3\cdot 9H_2O$	0	2	1	2	3	O_h	$Cs_2NaYF_6:Eu^{3+}$	0	1	0	0	0
C_4		1	2	2	3	5	I_h		0	1	0	0	0

[a] Electric dipole selection rules are given for $^5D_0 \rightarrow {}^7F_{0,2,3,4}$ whereas magnetic dipole selection rules are given for $^5D_0 \rightarrow {}^7F_1$. The $^5D_0 \rightarrow {}^7F_3$ transition is forbidden under the Judd forced dipole *SLJ* selection rules, but can appear weak if allowed by the site group selection rules. The $^5D_0 \rightarrow {}^7F_0$ transition can occur through *J*-mixing. [b] oda oxydiacetate.

Ref. : P.A. Tanner, Chem. Soc. Rev. 42 (2013) 5090.



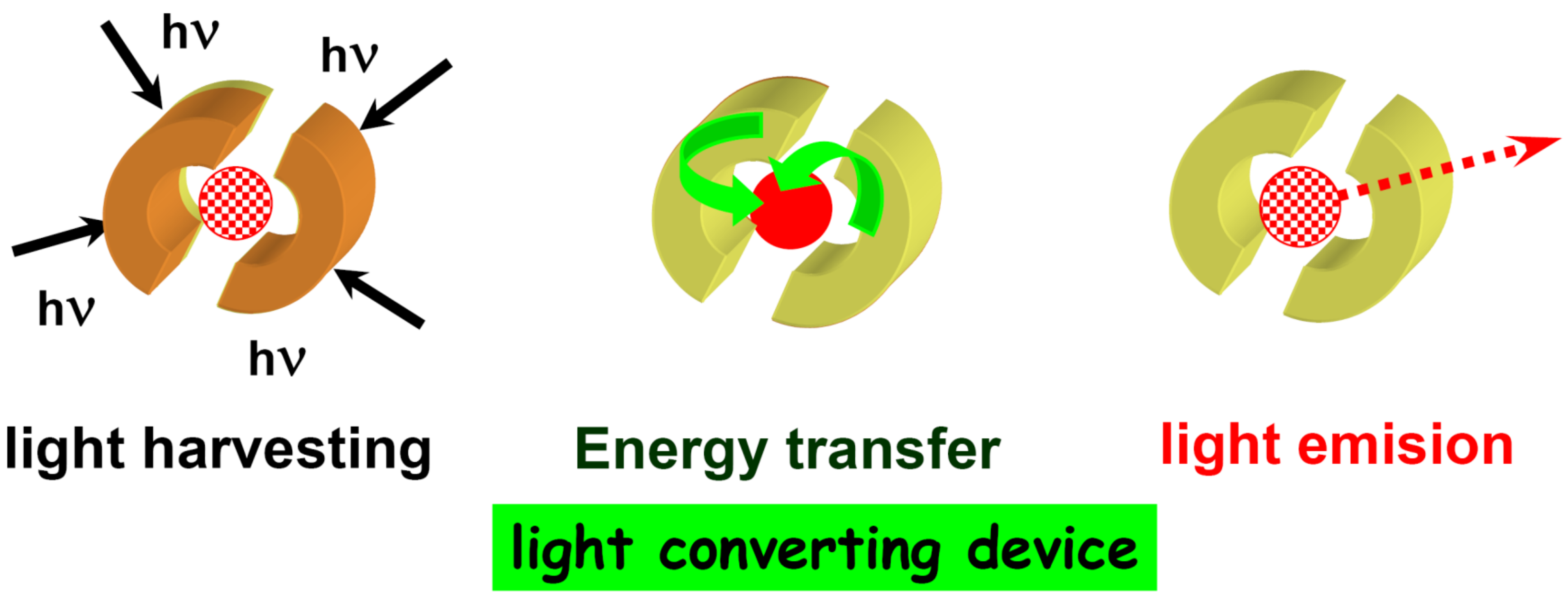
Ref. : J.C.G Bünzli, redrawn after K. Binnemans and C. Görller-Walrand, Journal of Rare Earths 14 (1996) 173.

Eu^{3+} as a probe for site symmetry determination

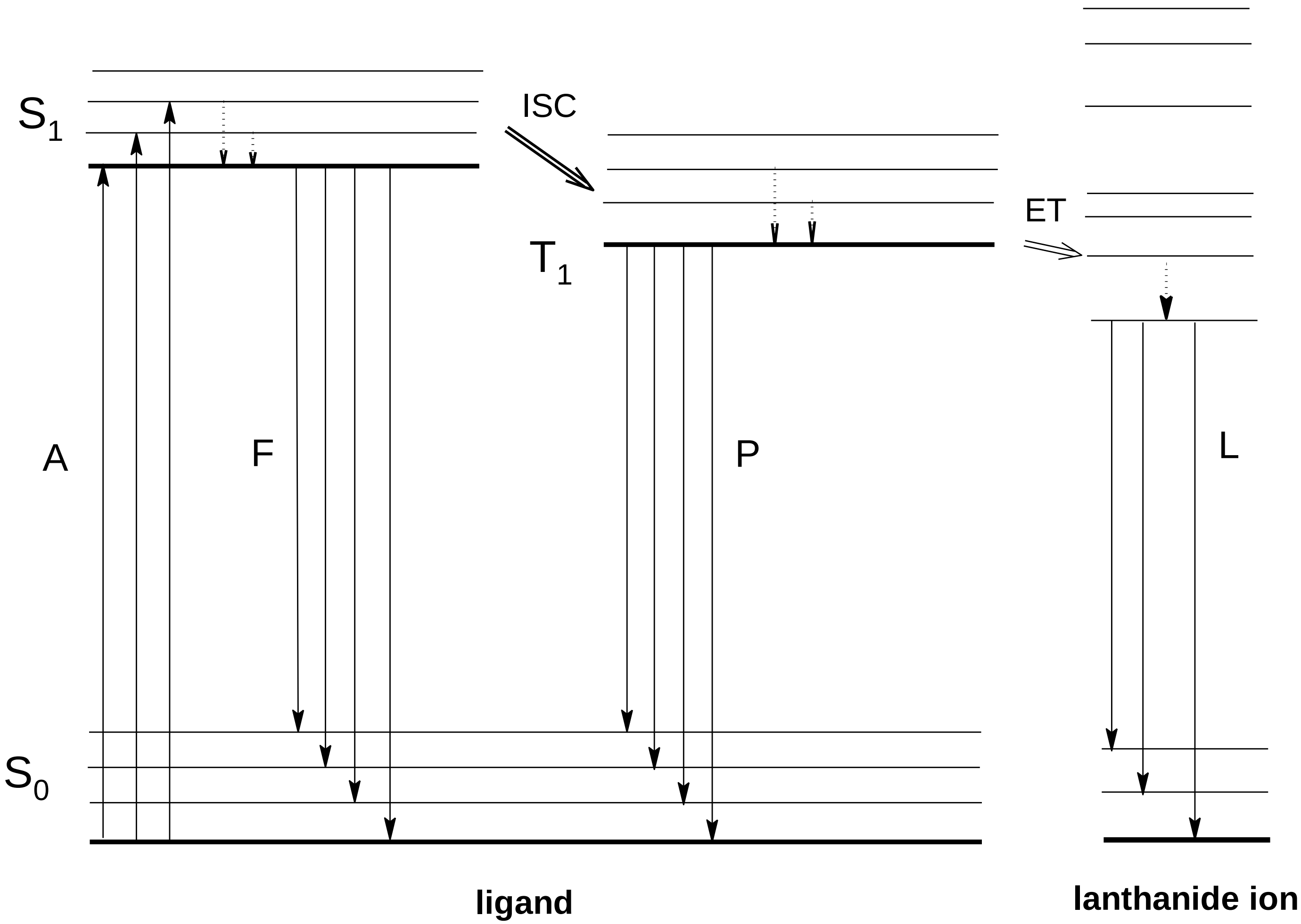
- In principle, it is possible to determine the point group symmetry of the Eu^{3+} site by counting the number of CF components that can be observed for the transitions $^5D_0 \rightarrow {}^7F_J$.
- In practice, an unambiguous assignment of the point group symmetry on the basis of the number of observed CF components is difficult.
  - Overlapping transitions (in case of small CF splitting or low resolution)
  - Extra lines due to vibronic transitions or crystal defects
  - Overlap with transitions from $^5D_1$ and $^5D_2$

Antenna effect

- Weak light absorption by forbidden f-f transitions; molar absorption coefficients ε are < 10 L^{-1} mol cm^{-1}.
- Indirect excitation via attached ligands or via host lattice in order to get sensitized luminescence.
- Excitation energy is transferred from ligand to lanthanide ion.



Antenna effect

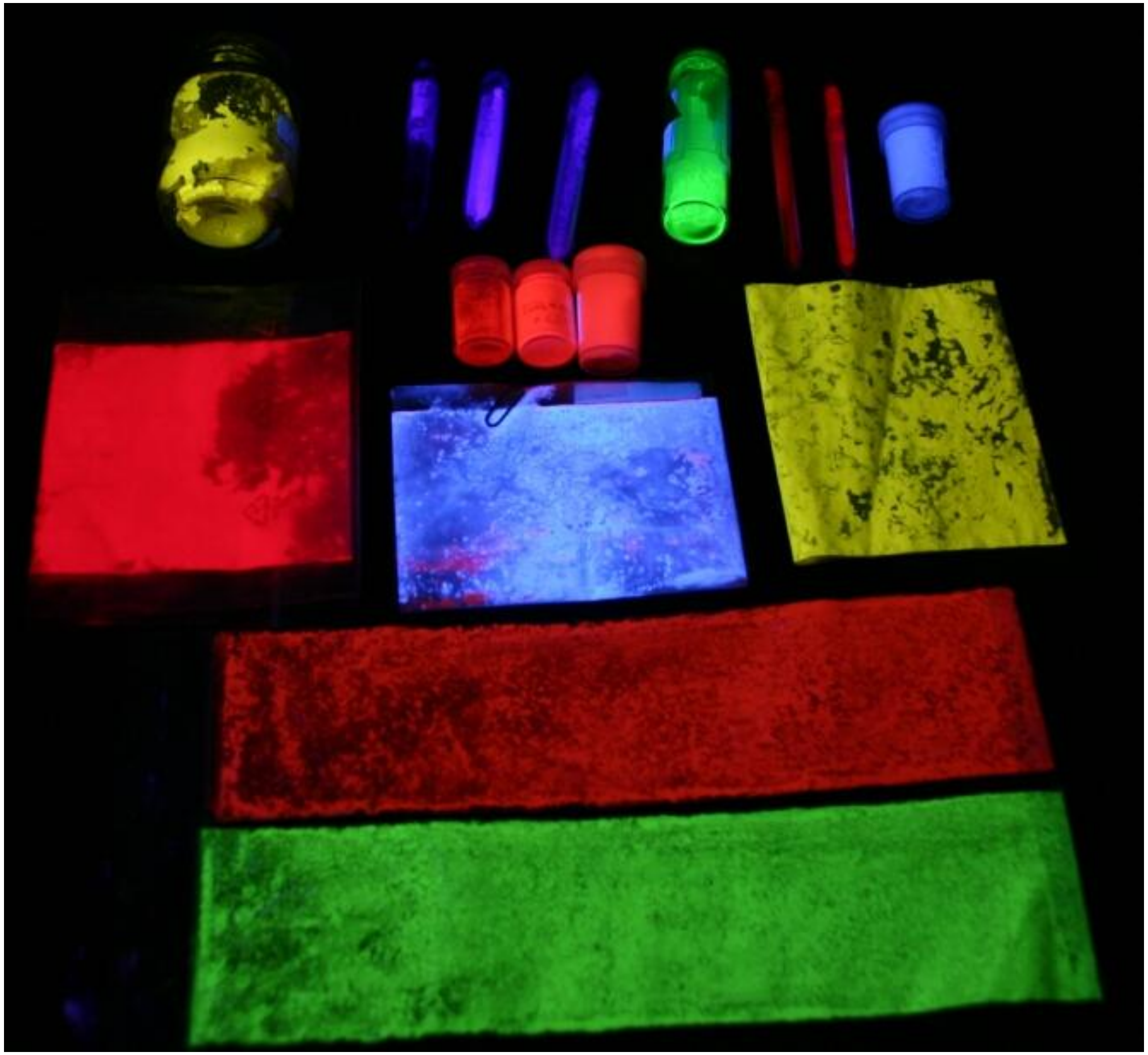


A = absorption, F = fluorescence, P = phosphorescence,
L = lanthanide-centered luminescence, ISC = intersystem crossing,
ET = energy transfer; S = singlet, T = triplet.

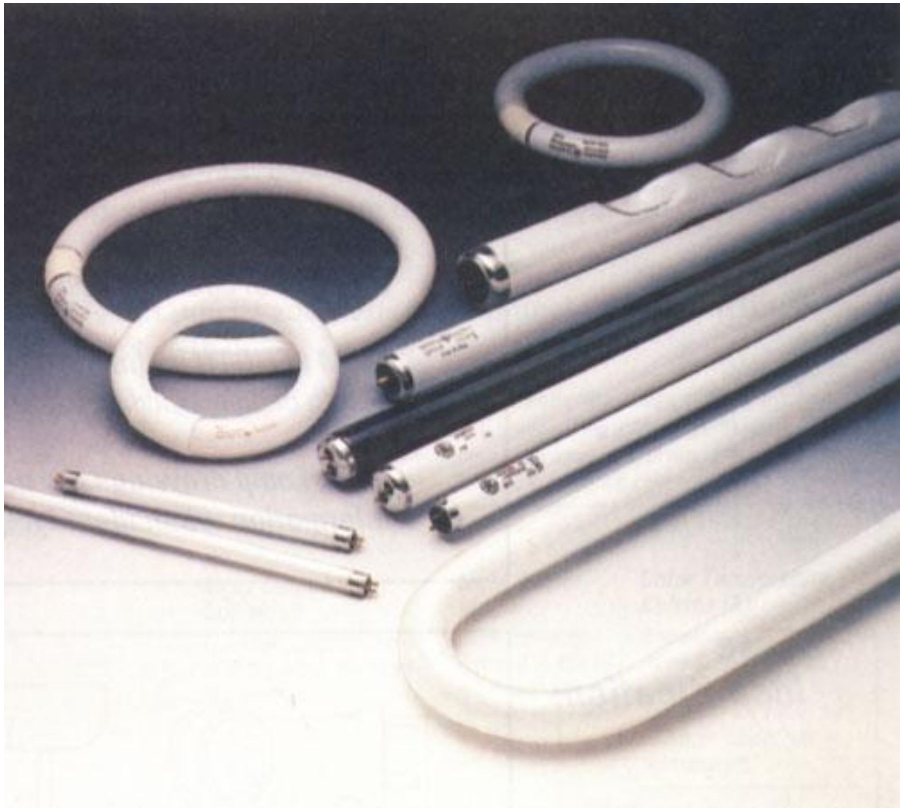
Other routes to sensitization

- Sensitization is not only possible via energy transfer from triplet state of organic ligands, but also by:
  - Inorganic chromophores (e.g. MoO_4^{2-}, VO_4^{2-})
  - Charge-transfer bands

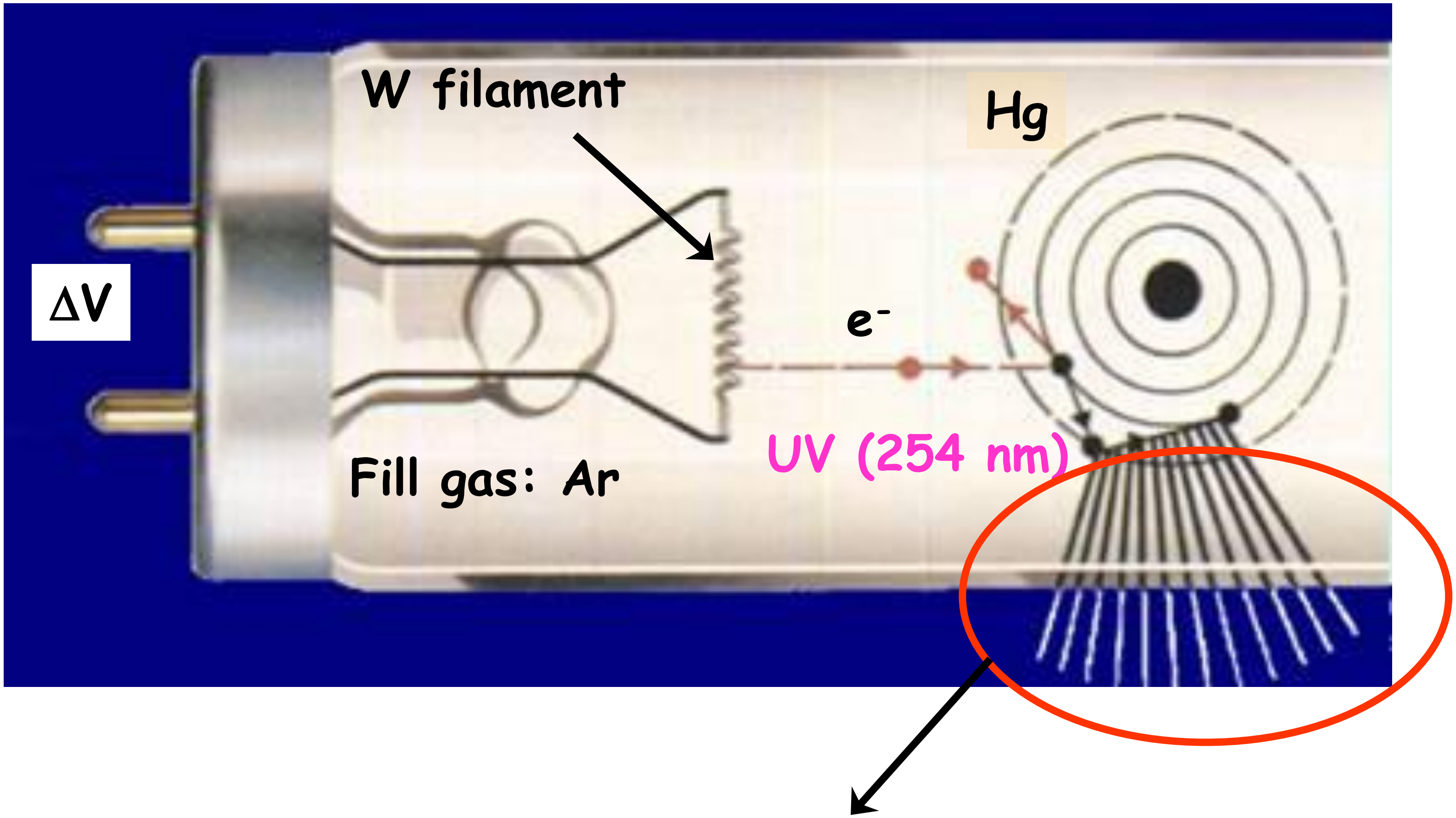
Lanthanide phosphors



Fluorescent lamps

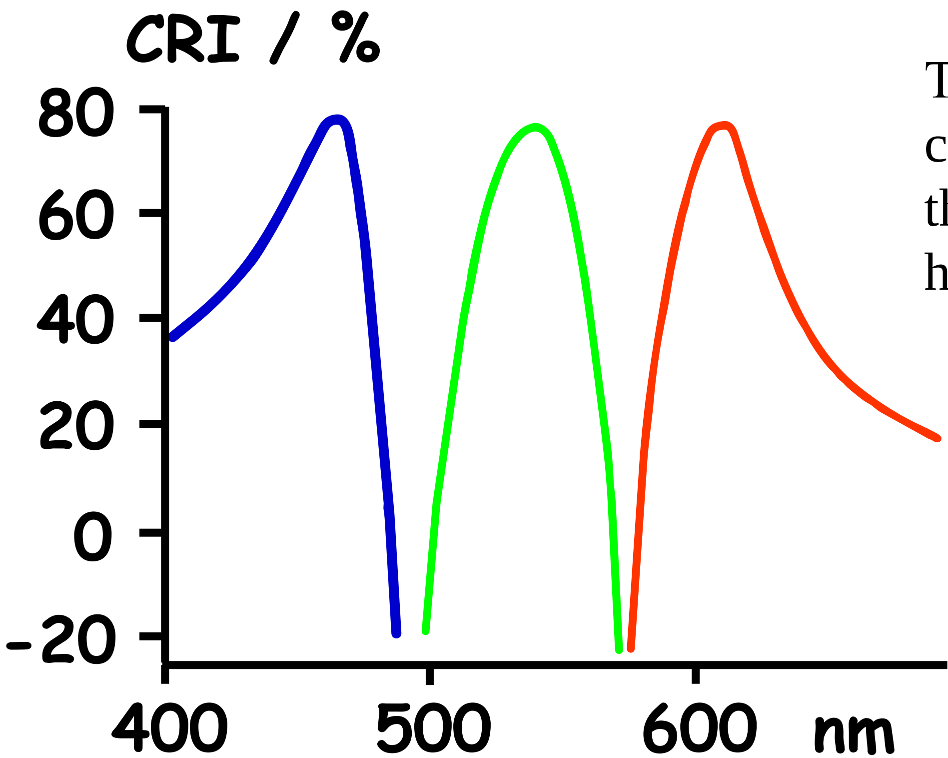


Fluorescent lamps

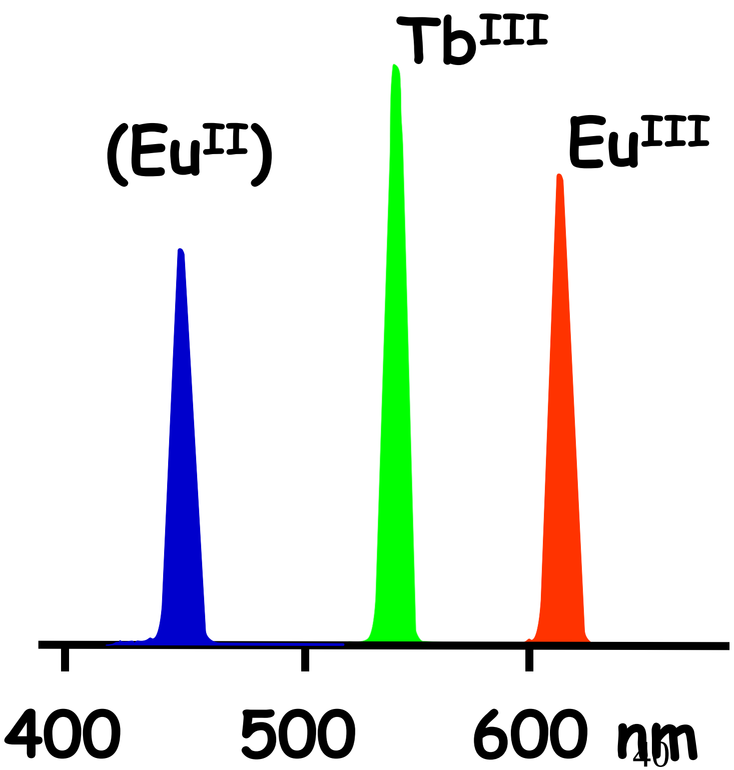


UV photons excite phosphor coating. White light is emitted by blend of phosphors

Producing white light: trichromatic stimuli



There are three "prime" colors corresponding to the three spectral responses of human vision



Color rendering index obtained by mixing the three prime colors

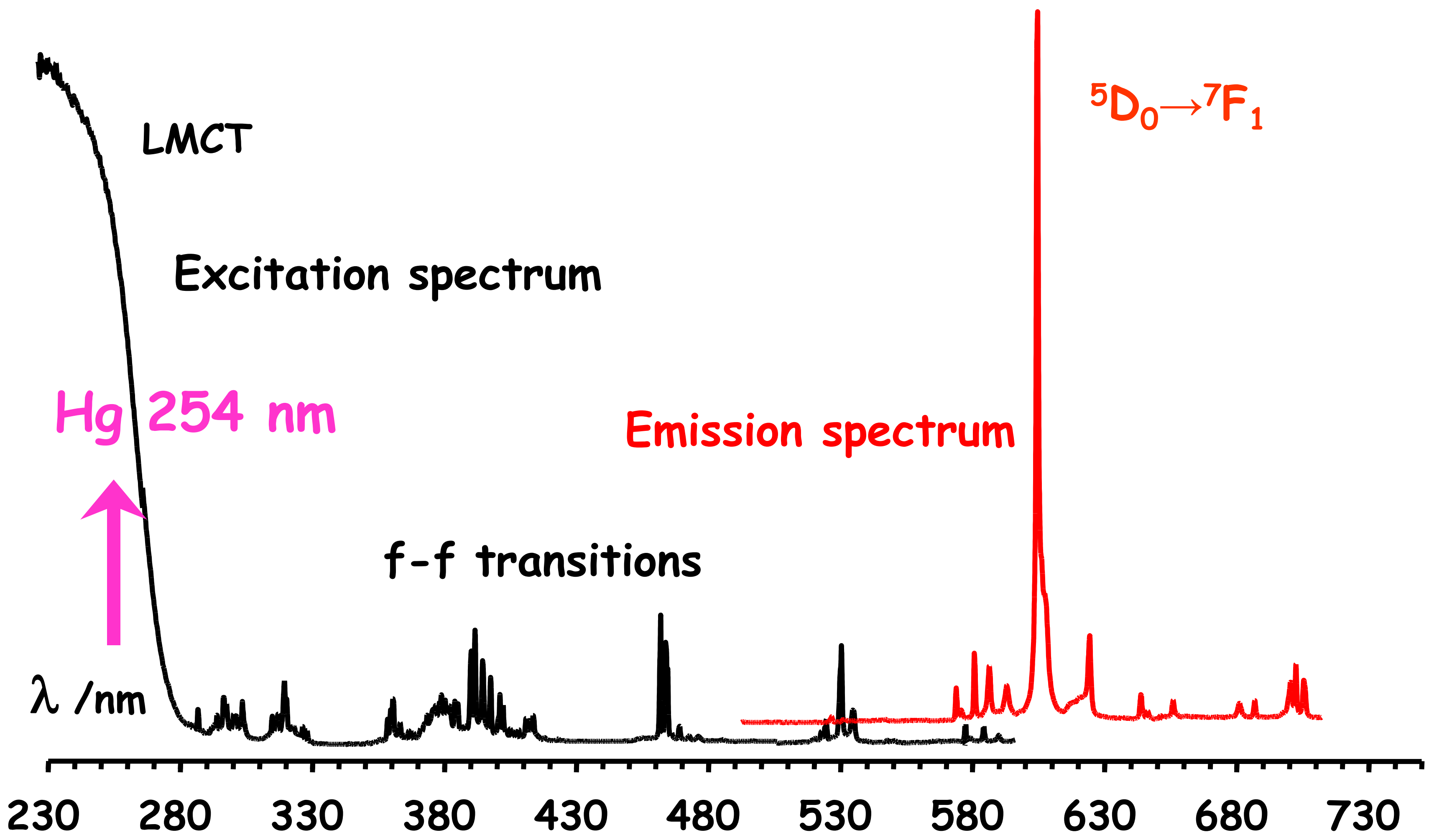
Ref. : J.C.G Bünzli, Lanthanide course

Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

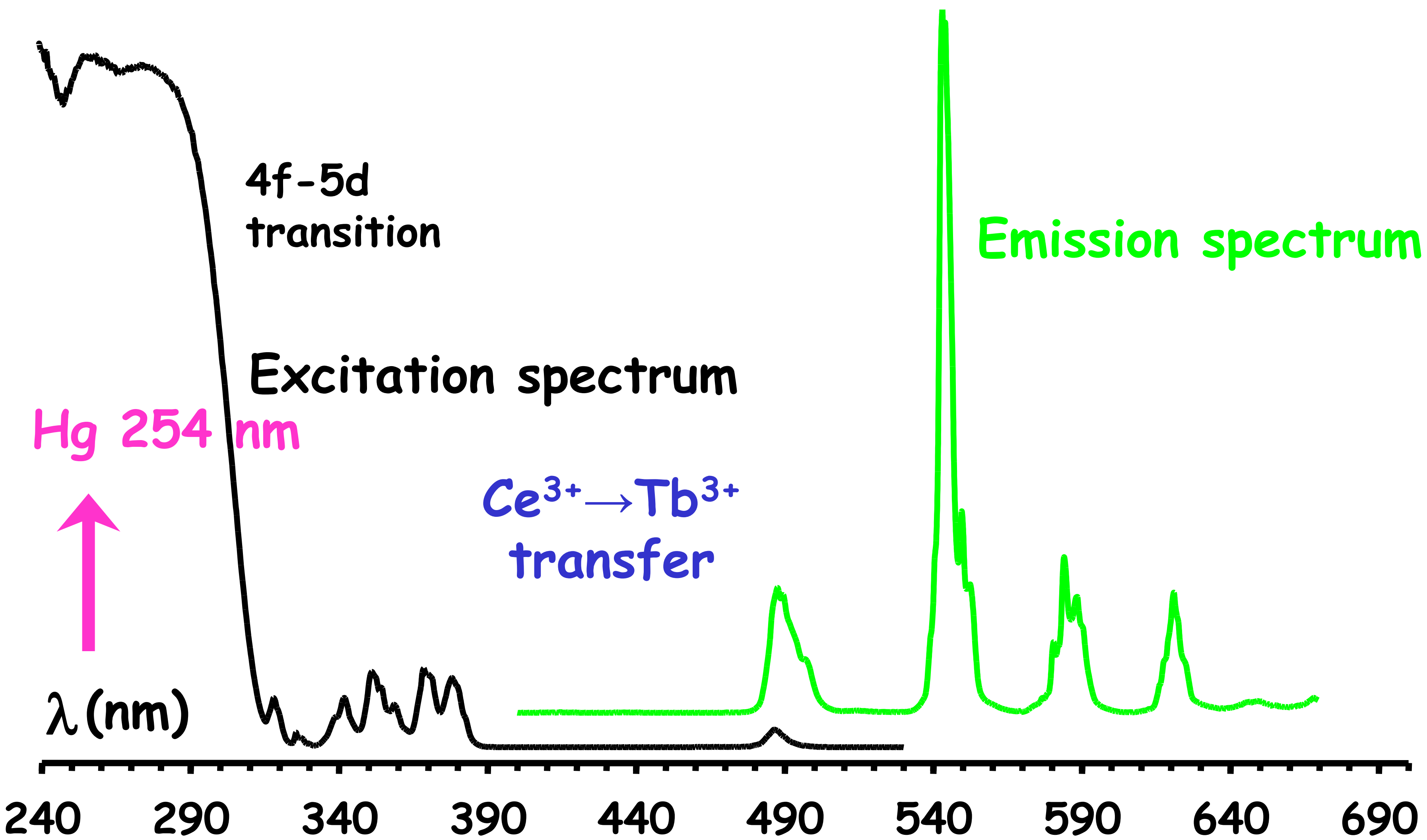
Ref. : J.C.G Bünzli, Lanthanide course

Red phosphor $Y_2O_3:Eu^{3+}$



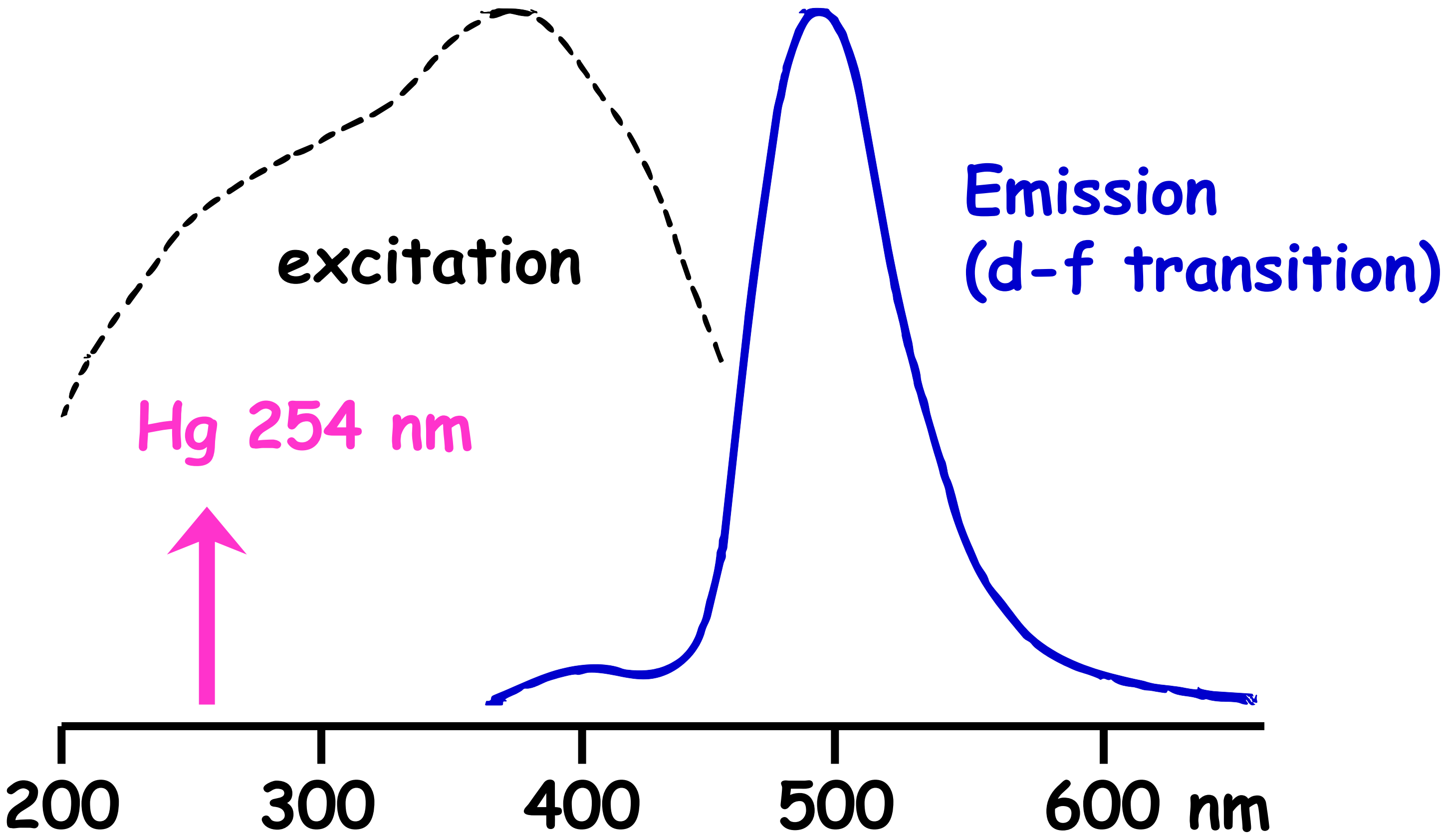
Ref. : J.C.G Bünzli, Lanthanide course

Green phosphor $LaPO_4$:(Ce^{3+},Tb^{3+})



Ref. : J.C.G Bünzli, Lanthanide course

Blue phosphor $Sr_4Al_4O_{25}:Eu^{2+}$



Ref. : J.C.G Bünzli, Lanthanide course

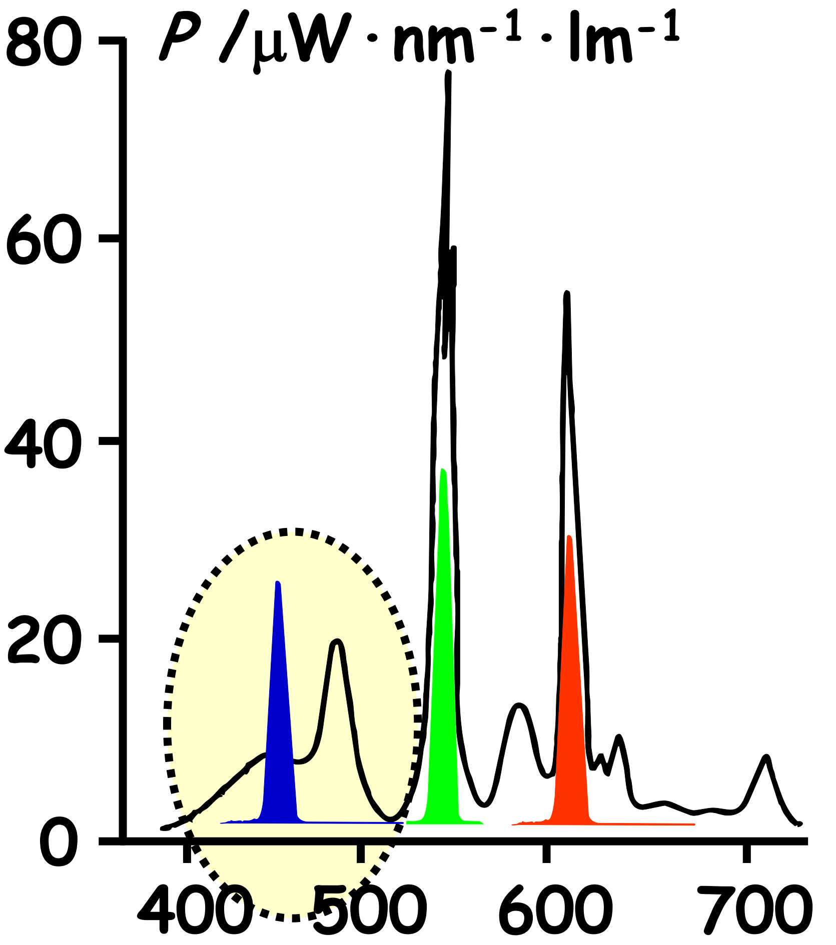
Tricolor lamps

Spectral distribution of a luminescent lamp with the following phosphors:

$BaMg_2Al_{16}O_{27}:Eu^{2+}$

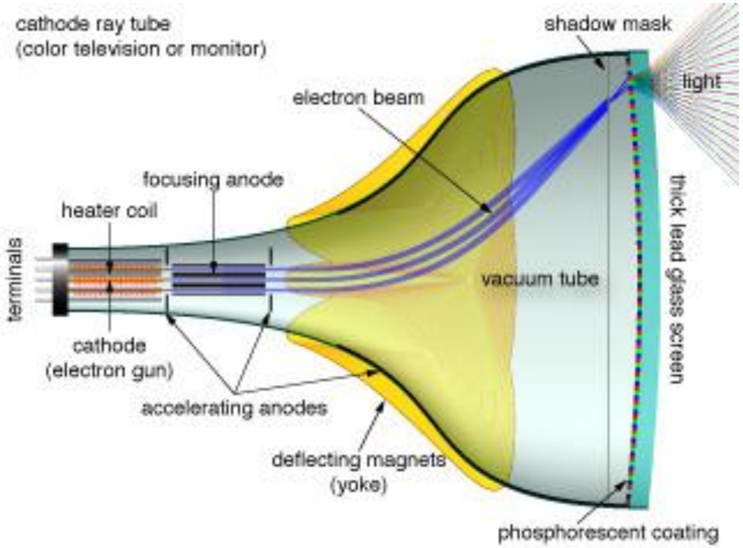
$CeMgAl_{11}O_{19}:Tb^{3+}$

$Y_2O_3:Eu^{3+}$



Ref. : J.C.G Bünzli, Lanthanide course

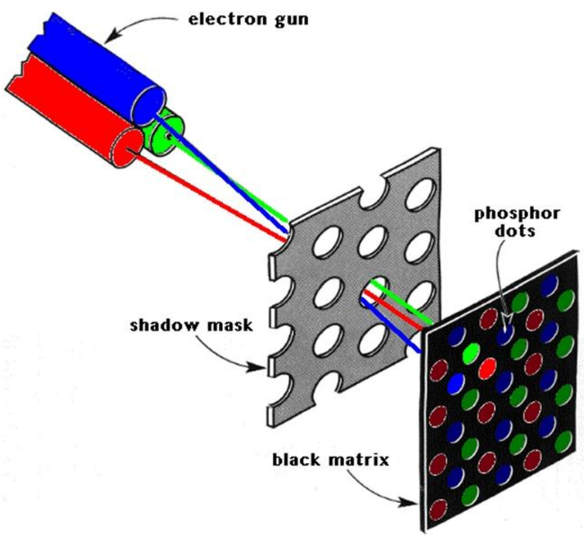
Cathode ray tubes (CRTs)

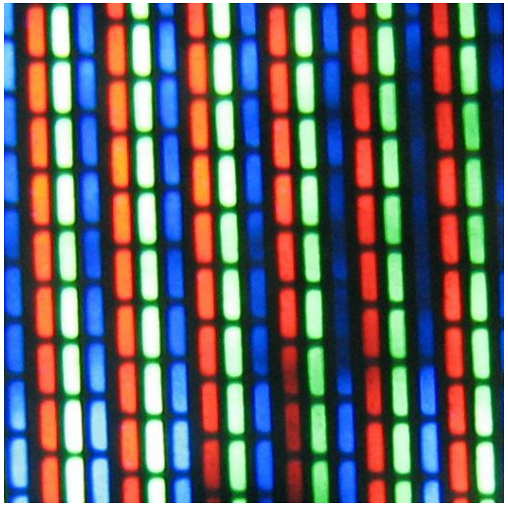


Red: $Y_2O_2S:Eu^{3+}$

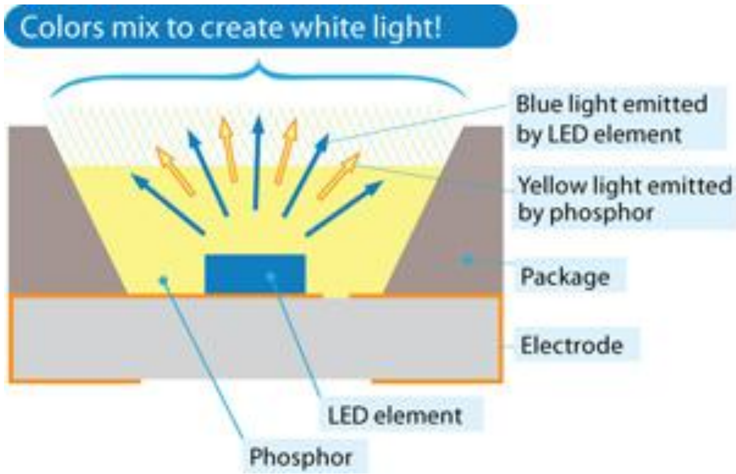
Green: ZnS:Cu

Blue: ZnS:Ag

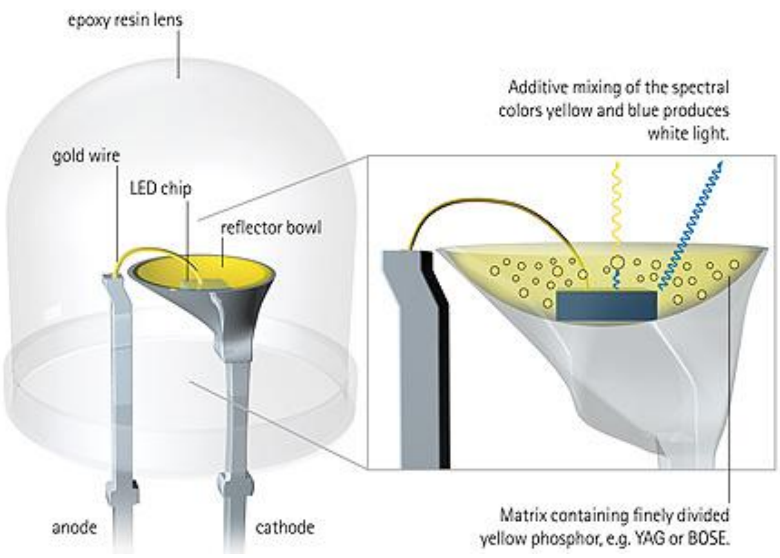


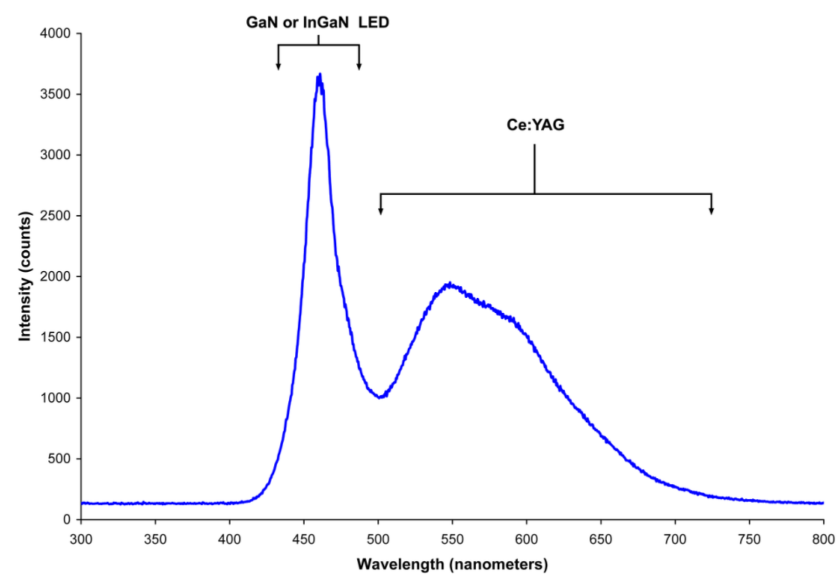


Phosphor-based white LEDs



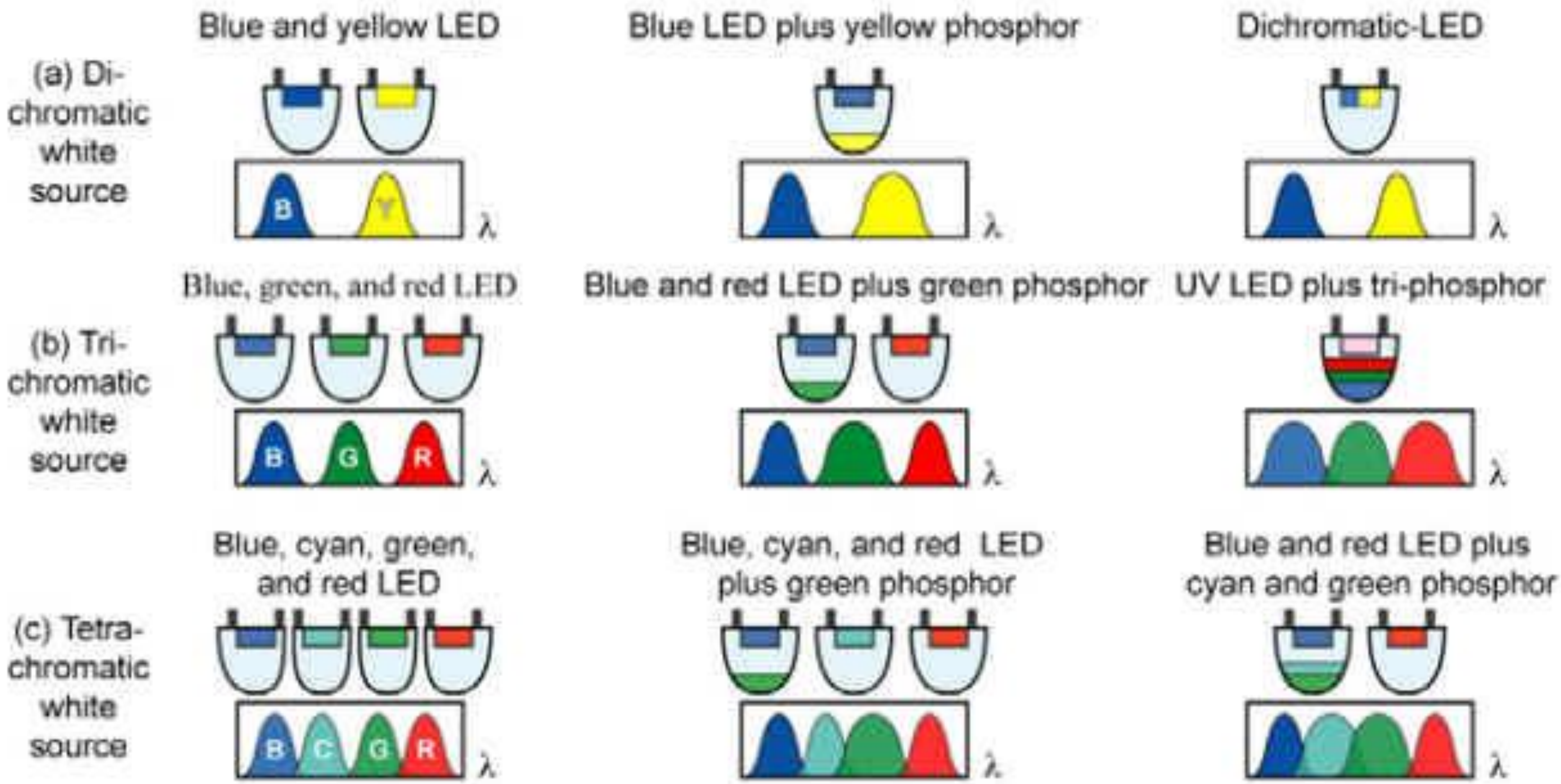
Combination of blue LED and yellow phosphor $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) gives (cold) white light





Source: Merck + Wikipedia

Different options to create white LEDs



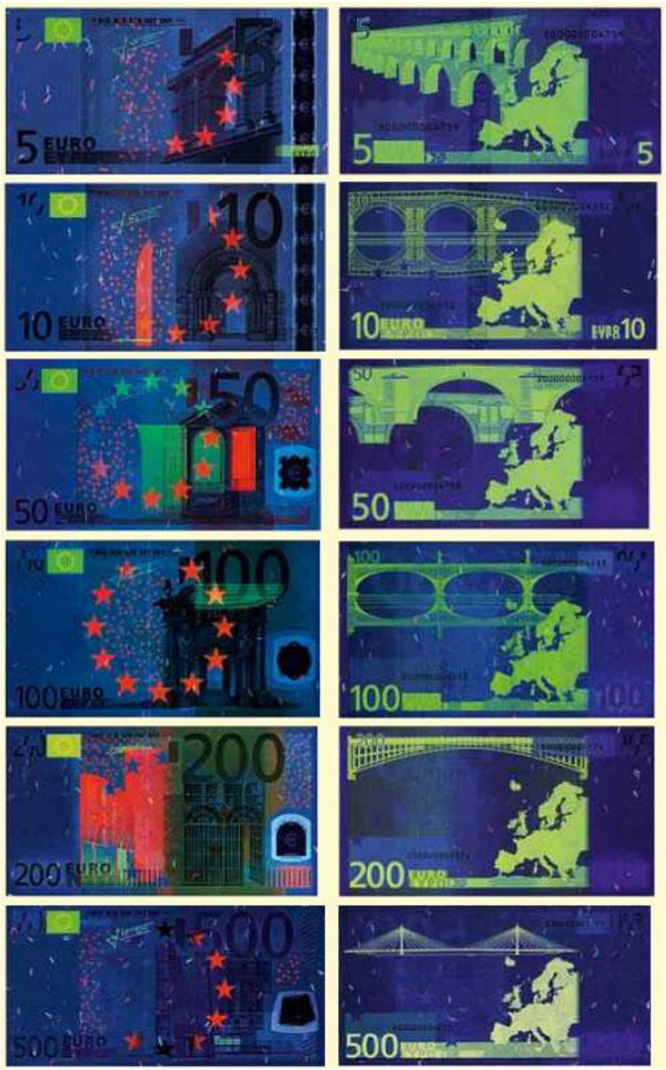
Source: http://pglab.nolda.co.kr

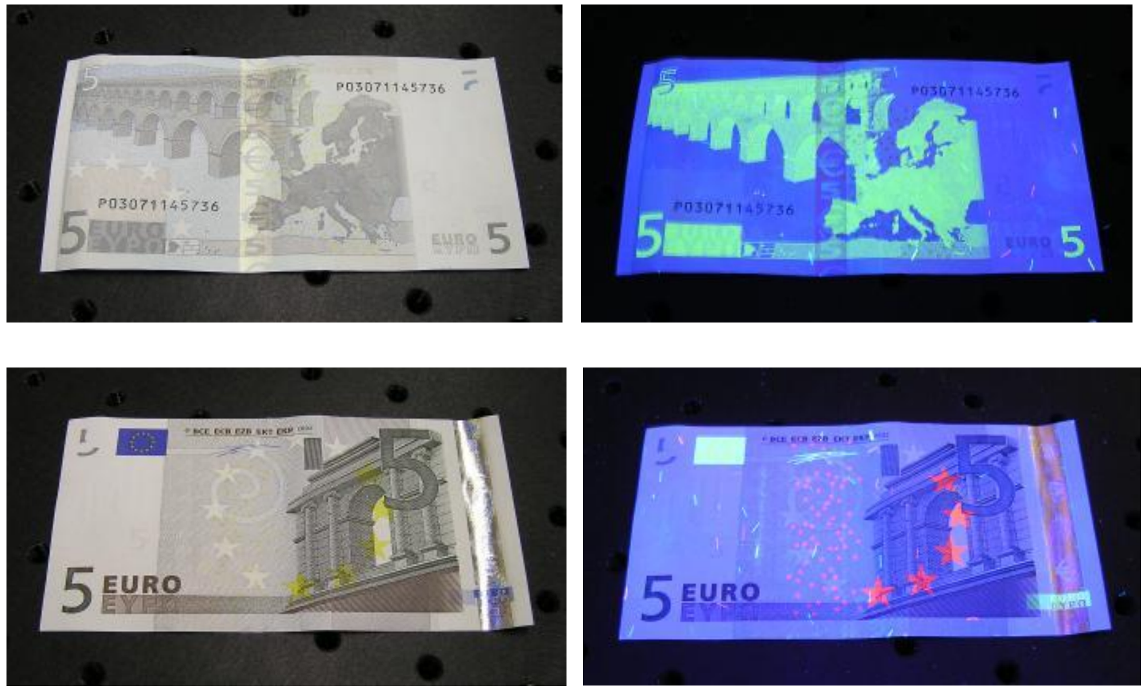
Security inks

UV

Euro bills

Security inks



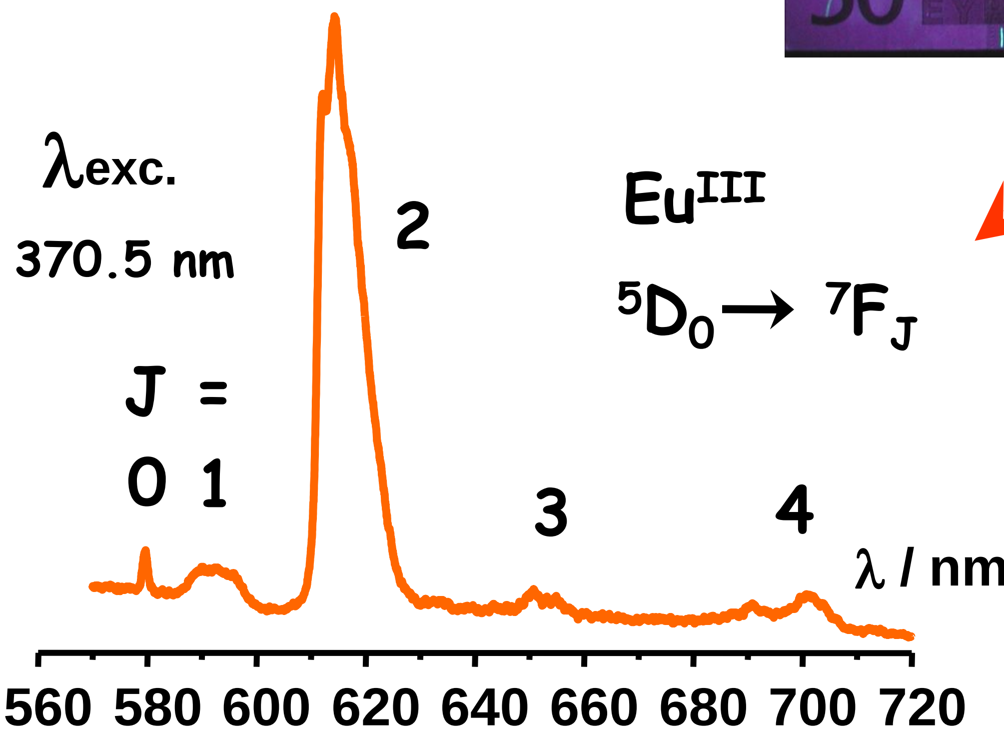


Under UV irradiation

Eu^{3+}: red luminescence

Eu^{2+}: green-yellow luminescence

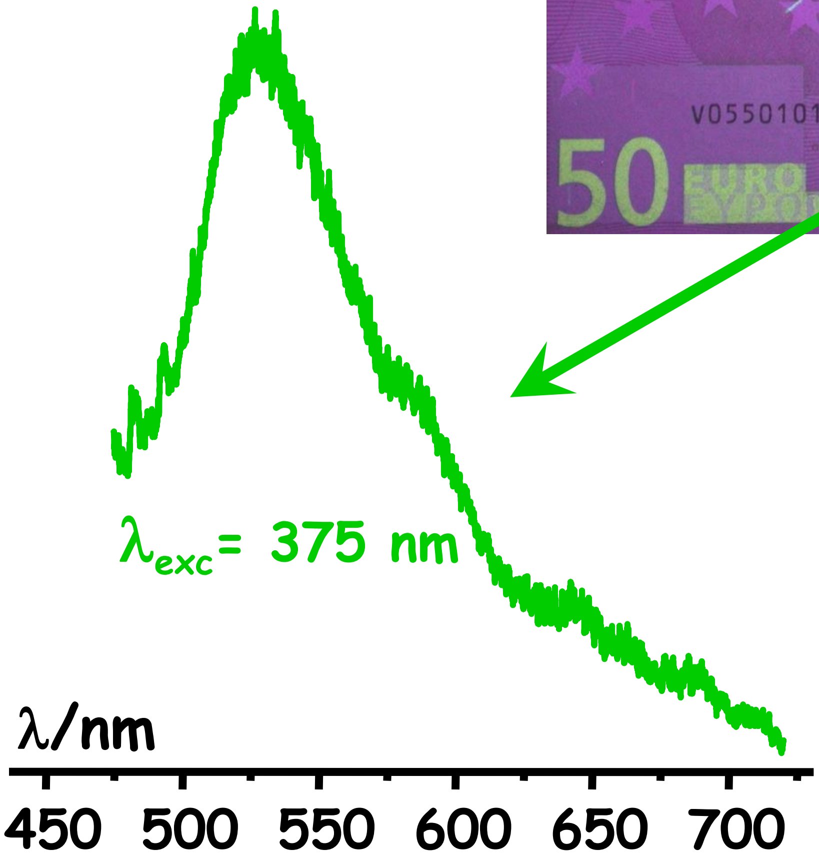
The euro is protected by the luminescence from europium: red from Eu^{3+}



Spectrum resembles that of a β-diketonate complex

Ref. : J.C.G Bünzli, Lanthanide course

Possibly Eu^{2+} ?



X-ray phosphors

- Designed to respond to X-rays re-emitting the energy as visible light
- Incorporated into a variety of X-ray imaging devices

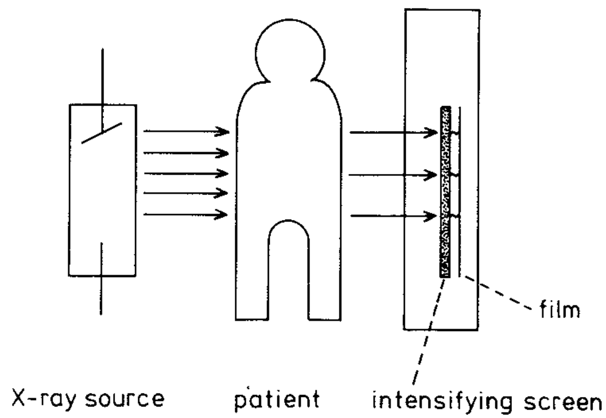
  Medical and security applications
- Most used phosphors:

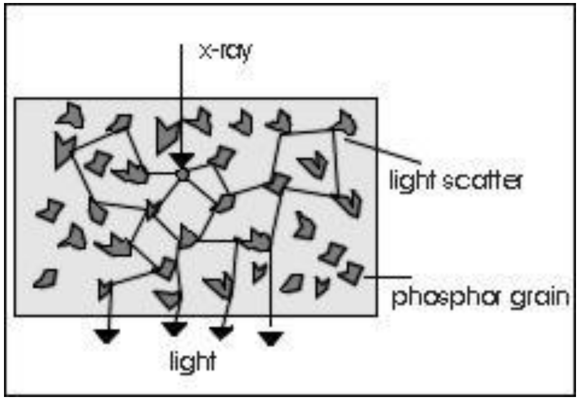
  $Gd_2O_2S:Tb^{3+}$ green

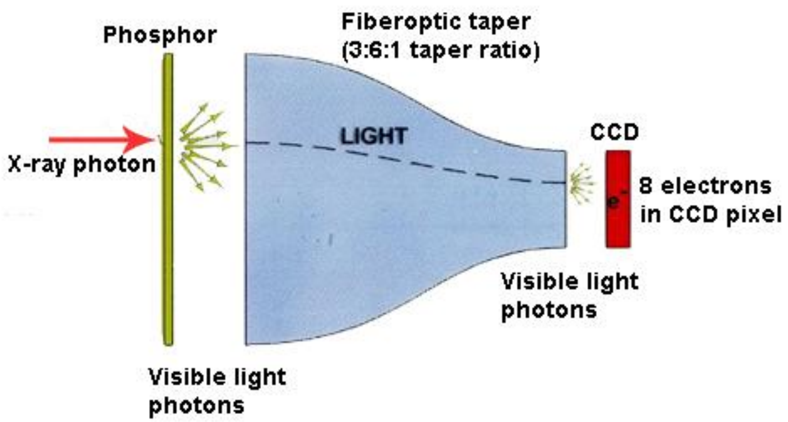
  $La_2O_2S:Tb^{3+}$ green

  $Gd_2O_2S:Pr^{3+}$ green

  $Gd_2O_2S:Eu^{3+}$ red





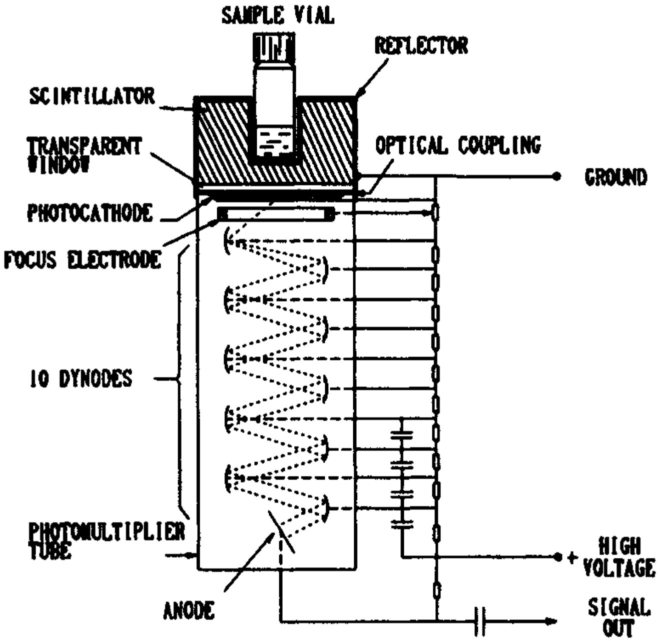


Scintillation phosphors

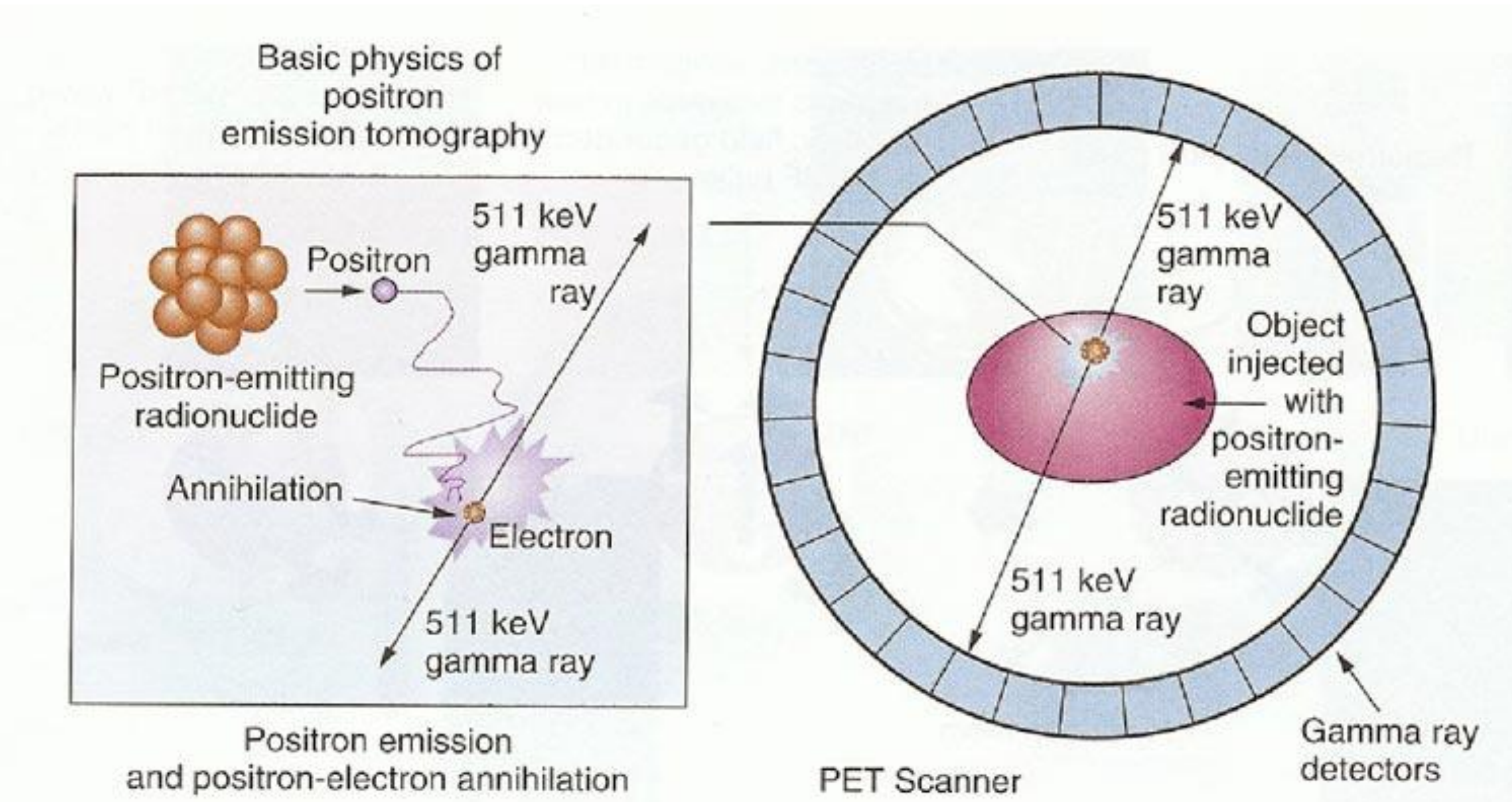
- Used in the detection of alpha, beta and gamma radiation
- Need to have fast decay times (40-65 ns) and high densities
- Most used phosphors:

$Lu_2SiO_5:Ce^{3+}$	peak: 400 nm
$YAlO_3:Ce^{3+}$	peak: 365 nm
$Y_3Al_5O_{12}:Ce^{3+}$	peak: 550 nm

- Use of $Lu_2SiO_5:Ce^{3+}$ in PET scanners is most important application of lutetium

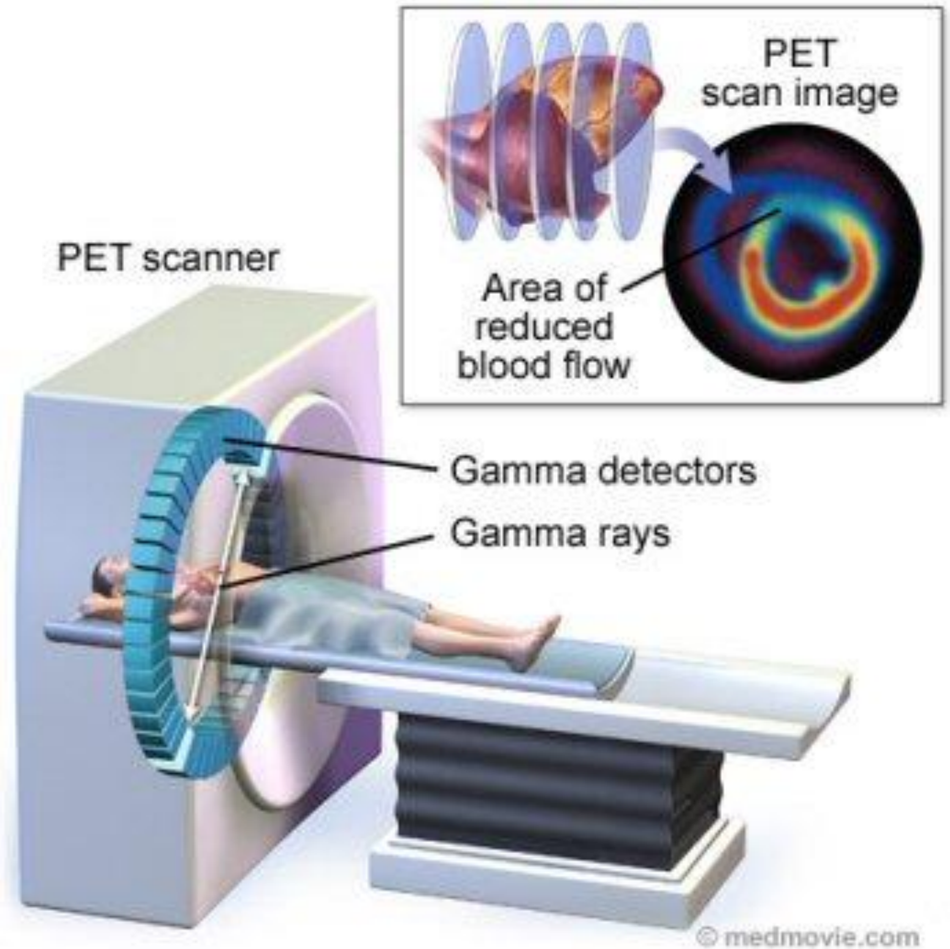


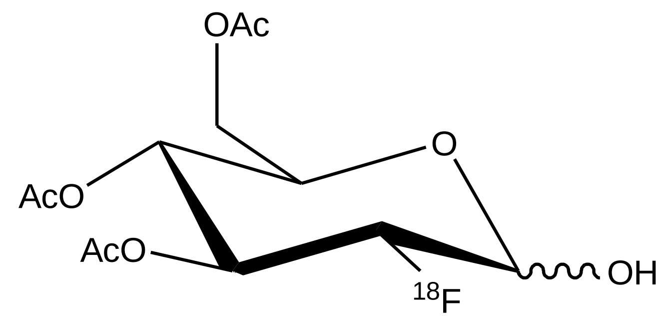
PET scanner



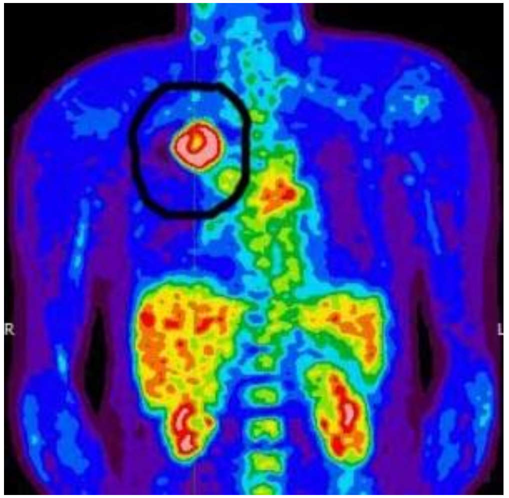
Source: http://www.cellsighttech.com

PET scanner





Positron emitter (^{18}F)



Detects increased metabolic activity